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NUMBER TWO

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED IN FIVE ISSUES BY THE
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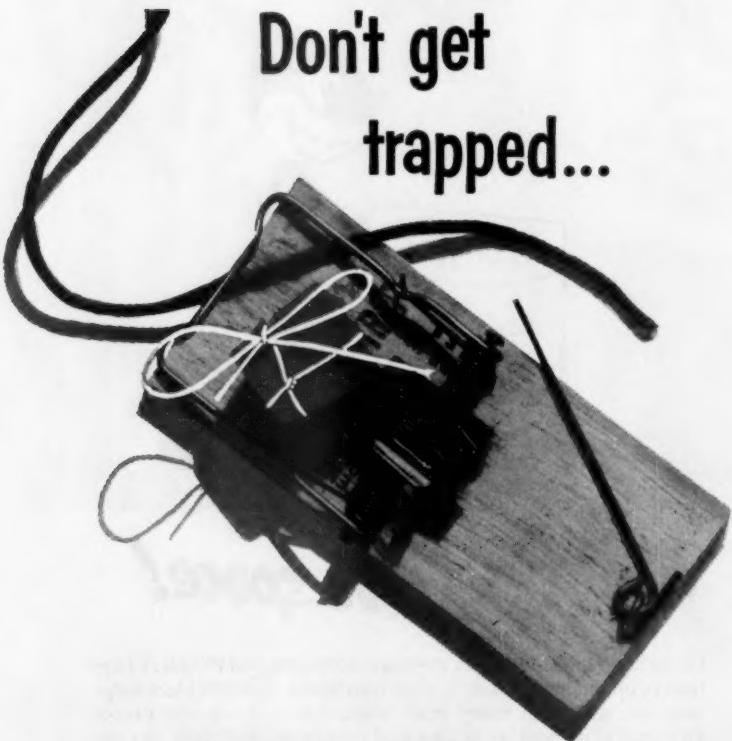


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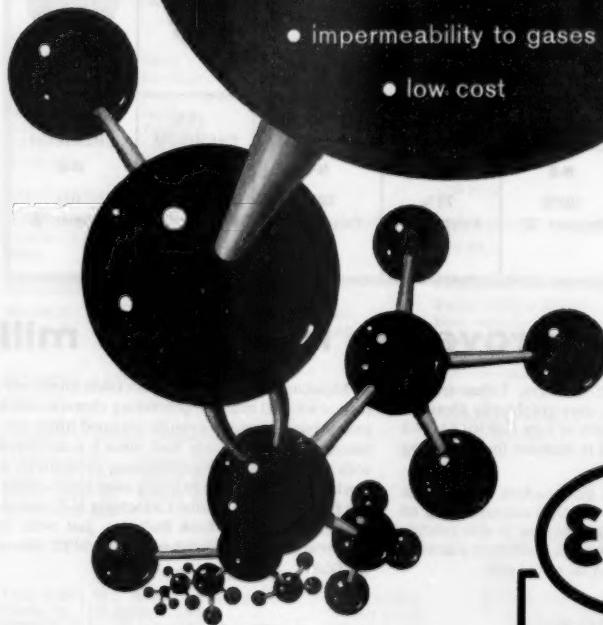
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Published by AMERICAN CYANAMID COMPANY, Rubber Chemicals Department, Bound Brook, New Jersey

NOBS No. 1 and NOBS Special Delayed Action Accelerators

The increased use of reinforcing furnace blacks together with high processing temperatures requires accelerators with a great degree of delayed action to insure safe compounding.

NOBS Special and NOBS No. 1 have been developed by Cyanamid's Rubber Chemicals Department to meet this requirement. They give excellent processing safety due to the built-in delayed action. In a natural rubber tread stock with HAF black, Mooney scorch times were determined with NOBS Special and NOBS No. 1 against NCBS (N-cyclohexylbenzothiazole-2-sulfenamide). The data indicate NOBS Special to have from 33% to 64% more delayed action and NOBS No. 1 to have from 21% to 48% more delayed action, depending on the sulfur ratio and processing temperature. The additional delayed action of NOBS Special and NOBS No. 1 results in no sacrifice in optimum cured physical properties.

NOBS Special is N-oxydiethylene benzothiazole-2-sulfenamide. The melting point range of 75-80 C. (167-176 F.) permits ready incorporation into furnace black stocks. Storage stability is good.

NOBS No. 1 is N-oxydiethylene benzothiazole-2-sulfenamide blended with a small amount of benzothiazyl disulfide. The melting point range of 70-75 C. (158-167 F.)

permits ready incorporation into furnace black stocks. Storage stability is good.

The general chemical and physical properties, specifications and compounding characteristics of NOBS Special and NOBS No. 1 Delayed-Action Accelerators are described in Cyanamid's Rubber Chemicals Bulletin No. 836A. Ask your Rubber Chemicals representative for your copy of this bulletin.

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A summary of the properties and uses of MBT and MBTS are to be found in Rubber Chemicals Bulletin No. 839. Ask your Rubber Chemicals representative for your copy of this bulletin.



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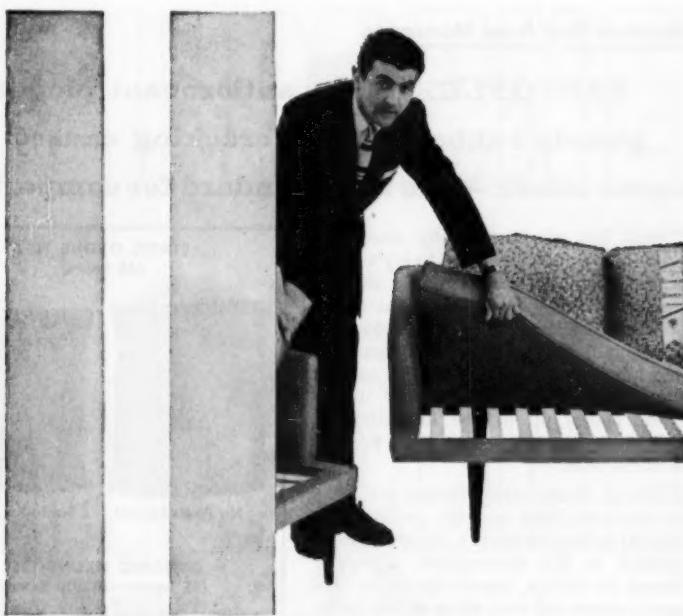
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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

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Meeting		City	Hotel	Date
1958	Fall	Chicago	Sherman	September 10-12
1959	Spring	Los Angeles	Biltmore	May 12-15
1959	Fall	Washington*	Shoreham	November 9-13
1960	Spring	Buffalo	Statler	May 24-27
1960	Fall	New York	Commodore	September 13-16
1961	Spring	Louisville	Brown	May 16-19
1961	Fall	Chicago	Sherman	September 5-8
1962	Spring	Boston	Statler	May 15-18

* An international meeting jointly sponsored by the Division of Rubber Chemistry ACS, Committee D-11 of ASTM, and the Rubber and Plastics Division of ASME.

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NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY, Volume XXI, 1957. Edited by T. J. Drakeley. Published by W. Heffer & Sons, Ltd., Cambridge, England, for the Institution of the Rubber Industry, 4 Kensington Palace Gardens, London, W.8, England. Cloth cover, $7\frac{1}{4} \times 9\frac{1}{4}$ inches, 146 pages. Price \$3.50.—With this volume, "Annual Report" attains its majority. Looking back over previous issues it is clear that the work has met a need, and as the industry has advanced and extended, and as new fields have opened up, this need has become greater than ever. It is surprising that, over a period of such tremendous developments including as it does those of World War II, the form of the present Report is almost identical with that of Volume I covering 1937, a tribute to Dr. Naunton who formulated the original plan. The only change is the comparatively small one of discussing together the chemistry of raw and vulcanized rubber, and of devoting a separate section to their physics.

A particularly welcome feature in recent years has been the promptitude with which the Report has appeared, always quite early in the year following that reviewed. This is due primarily to the strenuous efforts of the past Chairman of the Sub-Committee, Dr. C. F. Flint, and to the loyal cooperation of contributors, editor, indexer, and printer. To all these we acknowledge a debt of gratitude and we shall seek to live up to the reputation established. Throughout its twenty-one years the publication has had only one Editor,

namely Dr. T. J. Drakeley. What the industry, and the Institution, owe to his labors it is difficult to estimate but we take the opportunity afforded by this special occasion of tendering to him the congratulations and sincere thanks of the whole industry, at home and abroad. A most generous tribute must also be paid to the invaluable and unfailing assistance so willingly rendered over the past twenty-one years by the Research Association of British Rubber Manufacturers.

Readers will understand that no attempt is made to be comprehensive in the sense of including reference to every piece of literature. Contributors are invited to select, and to select critically, including only such matter as they deem constitutes significant progress. They are also invited to express their own views as experts in their particular fields. More comprehensive lists of references are available elsewhere to those who require them. To the general reader, the Report offers a convenient means of keeping informed as to progress in fields other than his own, and the specialist is given a second chance to appreciate the significance of a paper he may have underestimated at the time of publication. [Excerpted from the Foreword by T. H. Messenger.]

THE STORY OF EXPANDED RUBBER. By A. Cooper. Published by Expanded Rubber Company, Ltd., Croydon, England. Cloth cover, $5\frac{1}{2} \times 8\frac{1}{2}$ inches, 90 pages.—Although this book is ostensibly an account of the Expanded Rubber Company, the author has traced the history of expanded rubber from its beginning in 1905 when an Austrian printer, Robert Pleumer, started a search for a puncture-proof material for bicycle tires. The development of the story from this point and the trials and tribulations of the various companies that were formed, and that sometimes failed, during the following years makes fascinating reading and should be of interest to many students and technologists in the industry. [Reviewed in *Rubber and Plastics Age*.]

POLYSAR HANDBOOK. Volume I. Published by Polymer Corporation, Ltd., Sarnia, Ontario, Canada. Available in the United States from H. Muehlstein & Company, Inc., 60 East 42nd Street, New York, New York. Cloth cover, $6\frac{1}{2} \times 9\frac{1}{2}$ inches, 535 pages.—The book, published for private circulation, describes first the current six General Purpose Polymers (butadiene-styrene) and the properties of their vulcanizates in a section covering 135 pages. In the past, compounding formulas for synthetic rubbers have been based almost exclusively on the use of carbon black. Here the emphasis is rather on light colored compounds and the fillers to be used for these, thus enabling rubber manufacturers to turn out articles in line with modern styles and tastes. Under the heading Special Purpose Polymers the possibilities of the well-known high styrene rubber, Polysar SS 250, are well explored as well as S-X 371, a terpolymer for improved processing, and S-65 (now replaced by Kryflex 200), a special synthetic for cable insulation.

There is an excellent description of the oil resisting rubbers of which four types are offered, the uses of each being illustrated by numerous tables and diagrams. Butyl rubbers are dealt with in detail. There are now six different types at least one of which (Butyl 301) is finding applications outside the rubber industry, being used as an additive to improve the properties of conventional wax coatings.

The final descriptive section deals with the Polysar Latexes. In the lengthy and useful appendix the reader will find much general technical and other information and data not readily available elsewhere. There is for

example a table showing the resistance of the various types of synthetic rubber to a wide range of chemicals. Methods of testing are also given and care has been taken to include a description of the various accelerators, antioxidants, and other compounding ingredients mentioned in the main part of the book, together with the names and addresses of suppliers. Here, as would be expected in the case of a firm engaged in a world wide trade, the named suppliers are not confined to any one country so that users everywhere should be able to obtain what they require from the most conveniently available source. It would have been helpful to have had somewhere in the book a table showing the amounts of styrene, butadiene and acrylonitrile combined in the various rubbers. The wording "butadiene-styrene" under the heading monomers, for all of the many types of butadiene-styrene rubbers gives no information to the reader. [Reviewed by H. J. Stern in *Rubber Journal and International Plastics.*]

BRITISH COMPOUNDING INGREDIENTS FOR RUBBER. Compiled for the Research Association of British Rubber Manufacturers by B. J. Wilson. Published by W. Heffer & Sons, Ltd., 4 Petty Cury, Cambridge, England. 6 × 9 inches, 528 pages. Price \$8.40.—This publication contains only materials which are of British or British Commonwealth manufacture, or which receive a substantial proportion of their processing in the United Kingdom. As far as can be ascertained, all the materials listed are on the market at the time of going to press. Apart from the introduction, and a brief section listing specifications, the book is divided into four main parts, these being: Compounding Ingredients for Natural and Synthetic Rubbers; Compounding Ingredients and Processing and Modifying Agents Specifically for Natural and Synthetic Rubber Latexes; Special Purpose Products; and Indexes. The first three of these are again subdivided into sections dealing with various classes of chemicals. In each sub-section (e.g., sections such as accelerators, activators, antioxidants, coloring agents, fillers and reinforcing agents, blowing agents, odorants, retarders, etc.) the particulars given, e.g., broadly, as follows: Trade Name (in alphabetical order), Supplier, Chemical Composition, Function, Physical Properties, and Notes on Use. (These notes may be quite short, or reasonably comprehensive. Such annotations should be definitely useful.) The "Special-Purpose Products" section deals with such materials as Dusting and Anti-Tack Agents; Mold Lubricants; Reclaimed Rubbers, Solvents, etc., and there is an Index of "Manufacturers and Suppliers," and a Subject and Trade Name Index are also features. [Reviewed by Philip Schidrowitz in *Rubber Journal and International Plastics.*]

FREE RADICALS IN SOLUTION. By Cheves Walling. Published by John Wiley & Sons, Inc., 440 Fourth Avenue, New York 16, New York. Cloth cover, 6 × 9 inches, 643 pages. Price \$14.50.—The chief virtue of this book is that it compiles, in one volume, much of the literature concerned with the chemistry of free radicals in solution. The survey of the literature through June, 1956, appears quite adequate. The book is well organized, clearly written, and carefully edited. Extensive use is made of vinyl polymerization to illustrate the kinetics of radical chain processes and the relation between structure and reactivity in radical reactions. Other radical chain processes such as additions to double bonds, halogen substitutions, and autoxidation are also adequately discussed. A more sketchy treatment of non-chain processes in which radicals are produced is included. The skillful use of

thermodynamics and kinetics serves to simplify the explanation of many of the results rather than to confuse the issue as is often the case. Graduate work in mathematics or thermodynamics is not required to appreciate the contents of this book.

Certain sections will appear sketchy to specialists, but the adequate literature references make this book almost indispensable to both chemists and physicists, particularly those working in the field of polymers. It is recommended that scientists interested in free radical processes examine this book carefully with the ultimate aim of adding it to their personal library. I believe most will agree it will be a worthwhile addition, even at this price. [Reviewed by V. L. Folt in *Rubber World*.]

PROGRESS IN PLASTICS 1957. Papers and discussions at the British Plastics Convention. Edited by Philip Morgan. Published for "British Plastics" by Iliffe & Sons, Ltd., Dorset House, Stamford Street, London, S.E.1, England. Published in the United States by Philosophical Library, Inc., 15 East 40th Street, New York 16, New York. Cloth cover, $6\frac{1}{2} \times 10$ inches, 394 pages, 60 pages of plates. Price \$22.50.—This is a collection of papers and following discussions presented at the 1957 International Plastics Convention held at Olympia, London. As originally presented, the papers were in an abbreviated form, so in the book the respective subjects receive a much more comprehensive treatment. Eighteen papers in all are presented which are well illustrated with graphs, sketches and excellently reproduced photographic plates. Ten of the eighteen authors are British while the rest are from the United States and Germany. This lends a breadth of experience and point of view to the subject matter.

The book is organized in sections by an appropriate arrangement of the papers. The section titles are as follows: Polyolefins, Polythene, Polyvinyl Chloride 1, Polyvinyl Chloride 2, Extrusion 1, Extrusion 2, Injection Moulding 1, Injection Moulding 2, Material Developments and Glass Reinforced Plastics. Sections of the same title differ in definition of the subject such as product information and process information. Only the first paper, "Polymerization of Olefins," by H. Mark, deals with the subject of polymerization, and in this respect is out of character with the rest of the subject matter. The rest of the papers deal with physical properties of polymeric materials, compounding aspects or processing characteristics. The discussion material is well presented and contributes substantially to the individual subjects. A subject index adds to the general utility of the volume. [Reviewed for **RUBBER CHEMISTRY AND TECHNOLOGY** by C. F. Gibbs.]

A GUIDE TO PLASTICS. By C. A. Redfern. Published for "British Plastics" by Iliffe & Sons, Ltd., Dorset House, Stamford Street, London, S.E.1, England. Published in the United States by Philosophical Library, Inc., 15 East 40th Street, New York 16, New York. Cloth cover, $5\frac{1}{2} \times 8\frac{1}{2}$ inches, 150 pages, 17 colored charts. Price \$7.50.—This is the second edition of the book, the first having been published in 1951. As the title states, this is a guide and not a treatise in any sense. The book is designed for persons looking for the rudiments of knowledge in the various phases of plastics technology. It might serve as a text for a brief, semi-scientific course in plastics or as a guide for the technician or engineer requiring an elementary background in the field.

The subject matter is covered in five chapters as follows: Plastics Nomen-

clature; Raw Materials for Plastics; The Manufacture of Plastics Materials; The Fabrication of Plastics; The Properties of Plastics Materials. A bibliography of selected volumes by both British and American authors and an index concludes the volume. Flow diagrams of various classes of plastics are presented in some seventeen colored charts which carry the systems from starting materials to finished products. These diagrams are well developed and would be quite helpful to the individual seeking his information in a nutshell. Also included in the chapter on fabrication are numerous diagrams of fabricating machinery such as molds, presses, extruders, etc.

The book is well written and presented from the point of view of the engineer rather than that of the chemist. Chemical formulas and equations have been omitted deliberately. The presentation is based on British industry practice and nomenclature and so will be misleading in a few minor respects to practice in the United States. [Reviewed for **RUBBER CHEMISTRY AND TECHNOLOGY** by C. F. Gibbs.]

FRICITION AND LUBRICATION. By F. P. Bowden and D. Tabor. Published by John Wiley & Sons, Inc., 440 Fourth Avenue, New York 16, New York. Cloth cover, $4\frac{1}{4} \times 6\frac{1}{4}$ inches, 150 pages. Price \$2.25.—This book is another in the popular and authoritative Monographs on Physical Subjects published by Methuen and Company, Ltd., in England and by Wiley in the United States. The first chapter is a short, but interesting historical introduction to the subjects of friction and lubrication that runs all the way from the musings of Leonardo da Vinci to the present. Chapter 2 is concerned with the nature of solid surfaces and the real area of contact between them during sliding, a fundamental factor in the investigation of frictional phenomena. The validity of the "classical" laws of friction and discussions of surface damage, and the mechanism of friction are the concern of the following chapter. Chapter 4 discusses the important role played by surface films on friction and the very large adhesive forces obtained when the films are removed; while the next chapter deals with the surface temperature of sliding solids.

Chapter 6, on the friction of non-metallic solids, covers the frictional behavior of polymeric materials. The friction of rubber is found to depend on the load and the geometry of the surfaces involved.

The second part of the book, beginning with Chapter 8, deals with the behavior of lubricated surfaces, and mention is made of the development of synthetic lubricants made of phthalates, adipates, sebacates, and various silicone oils. Boundary lubrication is the subject of Chapters 9 and 10, and a general discussion of extreme pressure lubricants is given in the concluding Chapter 11. The book is well written and interesting. Each chapter contains references to more advanced material for additional reading, and there are no involved mathematics to cause difficulties for some readers. The book is designed for those with general rather than the specialized interest in the field of friction and lubrication. [Reviewed in *Rubber World*.]

ADDUCT RUBBERS: A VERSATILE NEW FAMILY OF ELASTOMERS *

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INTRODUCTION

Research and commercial developments in the field of reaction products of diene rubbers and simple nonpolymerizable chemical compounds have been on the wane since World War II, probably due more than any other cause to the fact that properties formerly sought in rubber derivatives can be more easily and cheaply attained in the ever-increasing family of olefin polymers. So far as is known, no truly *elastomeric* rubber derivatives have ever been commercialized, undoubtedly because of the comparative unavailability of coreactants which would lead to rubbery rather than resinous products.

The present paper describes the preparation and various properties of a versatile family of specialty rubbers which are derived from the free radical addition of low molecular weight alkyl mercaptans to conventionally prepared diene rubbers. By carrying out the adduct reaction under conditions where oxygen is purged from the system, there appears to be no significant degradation of the polymer molecules. Infrared studies of the adducts show formation of saturated thioether structures and elimination of double bonds in proportion to the amount of mercaptan taken up by the polymer.

At high extents of saturation, the products become very interesting from a commercial standpoint. Attainment of good aging, heat resistance, balance between low temperature properties and solvent resistance, low gas permeability, or ozone resistance, in one or another of the derivatives make them excellent candidates as competitors for the various specialty rubbers now available. The evaluations and comparisons with other polymers described herein were designed primarily to reflect the performance of the basic polymers themselves, and hence have been run mostly in gum stocks or in standard loaded recipes. Except for a few typical end-use stocks described at the end of the paper of the type of interest for military applications, no efforts are reported here on attempts to attain maximum performance under extreme conditions.

Prior work in the field of mercaptan-diene rubber adducts—that is, where simple alkyl mercaptans lacking any polar groups were involved—was centered largely in the early years of the 12-year long U. S. government-sponsored synthetic rubber program. Interest in the reaction appears to have been confined largely to its value in shedding light on the mechanism of free radical polymerization and on the structure of the polymer (relative proportion of external to internal double bonds, etc.). The most significant work is that of Marvel, Snyder and coworkers at the University of Illinois¹⁻⁴, Kolthoff and coworkers

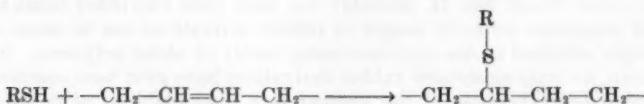
* This is a condensation prepared for RUBBER CHEMISTRY AND TECHNOLOGY of articles which appeared in *The Rubber and Plastics Age*, Vol. 38, July, pages 592-599; August, pages 708-721 (1957) and in *Rubber World*, Vol. 136, July, pages 529-536; August, pages 695-701 (1957).

at the University of Minnesota⁵⁻⁸, and the Standard Oil Development group under Swaney⁹⁻¹⁴. Except for routine examination of stress-strain, rebound, and flex properties, of a few 5-15 per cent saturated adducts by the latter workers^{9,14}, little or no interest appears to have been shown in the intrinsic properties of the reacted rubbers themselves. Pertinent patents in the field appear to be those of Swaney and Banes¹⁴, Swaney and Serniuk¹⁵, Fryling¹⁶, and Pritchard¹⁷, where interest appears to have been directed to use of the adducts as lube oil additives or as rubber plasticizers.

There has also been some reported interest in the mercaptan-olefin double bond addition reaction to confer specific polar groups using thioglycolic acid and like compounds¹⁸⁻²². The use of dimercaptans²³ and dithiol acids²⁴ for use as crosslinking agents for rubber has also received some attention.

PREPARATION OF ADDUCT POLYMERS

The basic reaction is



This is a highly simplified representation of a rather complex set of chain reactions involving several types of double bonds. Generally, the reaction is carried out in latex form, the appropriate stripped latex being charged to an evacuated autoclave along with the desired mercaptan (somewhat in excess of the amount needed to reach the desired saturation) and a free radical initiator, such as *bis*-azo-isobutyronitrile (AIBN). The reaction can be conveniently carried out at any of a variety of temperatures—usually in the range of 30 to 60° C, depending on the type of initiator and mercaptan used. The reacted latex is degassed, stripped, antioxidant added, then coagulated, washed, de-watered, and dried in essentially the same manner as used for processing SBR type rubbers. Except for a few reactions which were carried out in solution, all of the polymers referred to herein were prepared by this general technique. Inasmuch as the present paper is concerned primarily with the properties and structure of the polymers themselves, further details relating to their preparation are omitted.

TERMINOLOGY

The term "per cent saturation" is used throughout to denote the extent to which the *original* double bonds in the base polymer are presumed to be saturated with mercaptan, based on one or more analytical methods for measuring the amount of mercaptan added. Thus, a "50 per cent saturated adduct of methyl mercaptan and polybutadiene" would imply that $0.50 \times 48 = 24$ parts by weight of mercaptan had combined with 54 parts by weight of polymer to yield 78 parts of product. The adduct would then appear to have only $0.5 \times \frac{54}{78} \times 100 = 34.6$ per cent of the saturation value of the starting material, on a weight basis. The latter notation is not employed in this paper because its use makes too difficult the computation of the amount of mercaptan added or the fraction of double bonds reacted.

EXPERIMENTAL METHODS AND MATERIALS

METHODS

Measurement of extent of saturation.—Three methods were used for quantitative work: solids increase of the latex, refractive index increase of isolated and dried polymer, and sulfur content as determined by the Parr bomb method. Agreement was excellent when corrections were made for nonpolymer constituents (soap, etc.) that were present when solids measurements were made, but which were removed by purification for determinations of either sulfur content or refractive index. Virtually all the data on per cent saturation cited in this paper are based on Parr bomb determinations, except where otherwise shown.

Rate studies of methyl mercaptan-polybutadiene reaction.—Reactions were normally carried out in four-ounce bottles fitted with perforated metal screw caps and self-sealing gaskets, and were followed by solids increase or refractive index change. The reactants for reactions in latex were charged in the following order: (1) latex, (2) initiator in benzene solution, (3) methyl mercaptan. A slight excess of mercaptan was added to sweep out residual air in the bottle, and allowed to boil off. The capped bottles were rotated in a 50° C water bath. The reactions in solution were charged in the same manner substituting a benzene solution of polybutadiene for the latex. It was necessary in the latter case to sweep out the free space with nitrogen after charging the mercaptan, since the mercaptan dissolves readily in benzene.

For the photoinitiated reactions, the photosensitizer was added first, followed by the latex and mercaptan as above. The bottles were tumbled about six inches from a Westinghouse 275-watt sun lamp. The reaction temperature was 40° C and the course of the reaction was followed by solids increase. Control experiments were carried out in the dark with benzoin and in the light without benzoin.

Infrared analysis.—The instrument was a Perkin-Elmer Model 21 Double Beam Spectrophotometer. Both liquids and solids (films) were examined. The cells which contained the liquids had sodium chloride windows. For both liquids and films, a sodium chloride plate was inserted in the reference beam as a compensator. Operating conditions were: resolution, 927; response, 2; gain, 5; speed, 5; and suppression, 8. Films of the rubbers were laid down in $\frac{1}{8}$ inch $\times \frac{1}{4}$ inch frames by evaporation of 1 ml of three per cent benzene solutions.

General physical properties.—Stress-strain, Goodyear rebound, permanent set, abrasion, hardness, and the like were all run by standard rubber testing methods. Dynamic data were measured in the forced vibrator type of equipment described by Gehman and coworkers²⁵.

Oxygen absorption measurements.—The apparatus of Dr. J. O. Cole of this laboratory for measuring the rate of oxygen absorption is similar to that described by Shelton and Winn²⁶.

In the runs for which absorption by unprotected rubber are reported in this paper, all samples were pressed onto aluminum screening which had been washed in benzene. The thickness of the sample was 0.028 to 0.030 inch, or well under the thickness above which Shelton has determined that diffusion, as well as chemical reaction, begins to affect the rate of absorption. In runs in which the protective effect of antioxidants on adduct rubber were compared, the rubber sample was plated out on benzene-washed aluminum foil by evaporation of a benzene solution in an aluminum tray.

Potentiometric titration of disulfide in oxidized adducts.—Weighed portions

(1 gram) of the oxidized films out of the oxygen absorption apparatus were shaken with 50.0 ml of isopropyl alcohol for 24 hours, the bottles allowed to stand several days in the dark, and then aliquots of the extracts titrated for mercaptan and disulfide. The potentiometric titrations with silver nitrate were similar to those of Meyer²⁷ and of Cecil and McPhee²⁸. The indicating electrode was a solid bar of silver, and the reference electrode a Beckman glass electrode. A Model H-2 line-operated Beckman pH meter was used as the potentiometer.

Cure rate studies.—A masterbatch of all the curing ingredients was mixed with samples of a series of adducts covering the range of saturation from 0 to 95 per cent. The recipe contained 100 parts elastomer, 5 parts ZnO, 1 part stearic acid, 1.25 parts mercaptobenzothiazolyl disulfide, 0.25 part diphenylguanidine, 0.25 part methyl tuads and 1.25 parts sulfur. Samples were cured for various periods of time at 300° F and swelling volumes in benzene (as further described below) were determined to measure the extent of the cures.

Determination of solubility parameter μ .—Osmotic pressure measurements of benzene solutions of adducts of methyl mercaptan and polybutadiene were made at 25° C in Sands-Johnson-type osmometers. These data were used for calculating μ for benzene²⁹.

Swelling volume measurements for determining crosslink density.—Measurements for either quantitative or semiquantitative determinations of M_c , the molecular weight between crosslinks, were carried out by soaking 0.1 to 0.5 g portion of thin films in the appropriate solvent (usually benzene or *p*-xylene) for at least 40 hours, weighing the blotted film (enclosed in a vial), drying, and reweighing. Swelling data are reported on a volume/volume basis, i.e., volume of swollen material/volume of same material after drying.

Solvent swelling in fuels and lubricants.—These evaluations were run by the procedure described in ASTM D471-55T. The elastomers were cured in standard curing recipes.

Low temperature stiffening properties.—The torsional stiffness of elastomers at low temperatures (both gum stocks and loaded stocks) was measured by the method described by Gehman and others³⁰.

Heat aging tests.—Mechanical convection air ovens with temperature control of $\pm 10^{\circ}$ F were used for this work. Uncured samples were hot pressed (275–300° F) into sheet form (approximately 0.04 inch thick) which were free of bubbles and appeared uniform throughout. Groups of these sheets were placed separately on watch glasses for exposure in the oven and samples were withdrawn for examination at desired intervals. Standard tensile sheets of cured elastomers were cut into strips and hung separately in the oven for the desired periods.

Ozone resistance measurements.—A Mast ozone unit was used in which samples under both static and dynamic conditions were exposed simultaneously. The static samples were clamped at 20 per cent elongation and the dynamic samples were flexed from 0 to 28 per cent elongation at one cycle per second. In each case the samples were 1 × 6 inch strips cut from standard tensile sheets. The samples were inspected for degradation after 50 hours exposure to ozone at 50 ± 5 pphm at 100° F and at various periods thereafter.

Permeability to gases.—The hydrogen permeability determinations were made with a Cambridge Fabric Permeameter as described in ASTM D815-47. Air permeability was measured on films 0.030 inch thick and 10 inch diameter. The film was supported on the low pressure side by pumice stone and the amount of air going through the film under a differential pressure of 38 psi was measured volumetrically.

Gamma radiation exposures.—Portions of the raw elastomers, containing no added ingredients, were exposed to gamma radiation from a 2000 curie Cobalt 60 source at room temperature similar to the method described by the Goodrich group¹¹. Swelling volume tests in benzene were used as an indication of the extent of cure.

For irradiation of loaded stocks which had been cured by conventional means, for the purpose of evaluating their resistance to degradation, a method similar to that described above was used. Tensile and elongation characteristics were determined on portions of the samples before and after various periods of exposure.

Compatibility with other elastomers.—The method adopted was essentially that first proposed by Dobry¹². Briefly this consists of determining the concentration below which a solution of a pair of polymers (each at the same concentration) in a common good solvent exists as a single phase, and above which a separation into two phases occurs.

MATERIALS

Base polymers used for addition reaction.—Except for a few cases which are noted in the text, all of the base polymers used in this work were prepared in the standard "mutual" recipe and polymerized at 50° C: 100 parts of monomers; 180 parts water; 5.0 parts ORR soap flakes; 0.3 part K₂S₂O₈. When used as latexes (as was usually the case), either no shortstop or a very small amount—e.g., 0.025 to 0.05 part of sodium dimethyl dithiocarbamate—was added, and the latexes thoroughly stripped prior to use as a base material for addition of mercaptan. Where two monomers were used, the ratio shown is that in the charge.

Mercaptans.—Methyl mercaptan was used as received. Specifications are: purity—99 per cent min.; distillation range—4.5 to 7.5° C.; H₂S—0.2 per cent max.; methanol—0.1 per cent max.; cloud point—minus 30° F max.; color—water white. Rate comparisons made on a specially fractionated sample of this material showed no differences. Other thiols were used as received from the supplier, *n*-dodecyl, DDM, was regular synthetic rubber grade, not distilled, 14.0 per cent minimum mercaptan sulfur content.

Methyl octyl sulfide.—This was prepared by adding a mixture of 1- and 2-octene with methyl mercaptan using two parts AIBN as initiator at 50° C for 64 hours. The fraction from the second fractional distillation used for infrared study had the following properties:

TABLE I
PROPERTIES OF THE METHYL OCTYL SULFIDE USED

	This preparation	Reported for methyl- <i>n</i> -octyl sulfide ¹³
B.P. (17–18 mm)	83–84°	100.5–102.5
<i>n</i> _D ²¹	1.4557	1.457
Per cent Sulfur*	19.8	—

* Theoretical sulfur for CH₃SC₈H₁₇ = 20.0%.

The method of preparation and the sulfur content give assurance that the material is methyl octyl sulfide, but the boiling range suggests that it is a mixture of possible isomers.

INVESTIGATIONS ON REACTION MECHANISM
AND POLYMER STRUCTURE

GENERAL REMARKS ON KINETICS OF THE ADDITION REACTION

The overall kinetic picture for addition of a mercaptan to a typical diene polymer, such as emulsion polybutadiene, is exceedingly complex, being complicated by the facts that (1) there are three known double bond structures in the base polymer (*cis*-1,4; *trans*-1,4; and 1,2 units), (2) the free radical chain-like nature of the reaction implies that initiation, propagation, and termination reactions will be occurring simultaneously, each characterized by its own rate constant and differing in some instances for the various double bonds, (3) the greater technological interest in carrying the reactions to high saturation levels involves measurements in regions where values suitable for calculating kinetic constants are difficult to obtain.

With respect to the literature on kinetic studies of the reaction between mercaptans and simple olefins, the only significant work reported appears to be that of the Canadian group under Sivertz²⁴, who studied the addition of *n*-butyl mercaptan to styrene, 1-pentene, and isoprene. They discussed a series of reactions, initiation, attack, propagation and termination, which correlate with their results. A similar sequence of reactions is presumed to occur in the formation of mercaptan adduct polymers. In the latter case, the presence of three types of double bonds in the chain (*cis*, *trans*, and side vinyl) must necessarily lead to very complicated kinetics.

Because of the large number of concurrent reactions, no serious attempt to separate all the rate constants could be made. Rather, efforts were confined to making measurements which would be helpful in answering questions of practical importance, and in particular, the extent to which the kinetics resemble those of free radical polymerization.

RATE STUDIES WITH AZO-BIS-ISOBUTYRONITRILE

General studies on the addition reaction in emulsion were carried out to investigate the effect on reaction velocity of: (1) mercaptan concentration; (2) initiator concentration; (3) latex particle size and number of particles; (4) soap coverage of the latex particles.

Mercaptan concentration.—Since the overall reaction scheme of mercaptan addition is formally analogous to polymerization, the first efforts were directed toward detecting similarities in kinetics.

When the concentration range of methyl mercaptan was varied from 60 to 100 per cent of the amount necessary to saturate completely the double bonds of the polymer, curves of the type shown in Figure 1 were obtained, showing higher rates for the higher mercaptan charges. All the reaction appears to be taking place in the latex particles, since no separate mercaptan phase is visible at molar ratios of mercaptan: butadiene segment at least as high as 1:1. The initial reaction rate up to 10–15 per cent saturation is approximately first order with respect to mercaptan concentration.

Initiator concentration.—In “ideal” emulsion polymerization of dienes, an increase in initiator concentration after the particles have been formed, has in general no effect on the polymerization rate²⁵, whereas in solution or bulk polymerization, the rate is proportional to the square root of the initiator concentration²⁶. Two levels of AIBN concentration were investigated during preliminary exploration of the addition reaction. With a doubling of the initiator

(AIBN, 0.2 to 0.4 phr) no significant difference in reaction rate was observed. In control experiments to determine the effect of residual persulfate left over from the polymerization reactions (i.e., with no AIBN charged), the reaction was quite slow, yielding 5–15 per cent addition in 24 hours. Data were also obtained with a polybutadiene latex prepared with AIBN. From the first order disappearance rate of AIBN the amount left in the latex could be calculated. A charged amount of 0.95 phr AIBN gave the same rate of addition as previously obtained with 0.2 and 0.4 phr AIBN plus residual persulfate.

Reactions in latexes of varying particle size and in solution.—The effect of number of particles per cc of latex on the rate of emulsion polymerization has been well defined²⁷ and the proportionality demonstrated by several investigators^{28,29}. To determine the similarity, if any, of the mercaptan addition reaction with emulsion polymerization, the rate dependence of the addition reaction

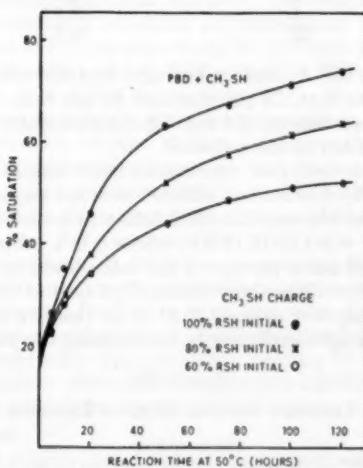


FIG. 1.—Typical reaction data with AIBN.

on number of particles was studied. Two latexes of equal solids content were prepared having particle sizes of 780 Å and 1040 Å (surface average diameters). The former therefore had twice as many particles as the latter. Carrying out the addition reaction under identical conditions (0.95 phr AIBN, 100 per cent theoretical MeSH for complete saturation), the larger particle size latex gave a slightly higher rate up to 55 per cent saturation (ca. 0.5 per cent per hour) than the smaller particle size latex. Therefore, the larger number of particles in the 780 Å latex did not increase the reaction rate.

Further to amplify the difference in dependence of adduction rate on latex particle size from the dependence of rate of emulsion diene polymerization, addition reactions were carried out in solution. The conditions which led to the results in Table II were: 6.4 per cent polybutadiene in C. P. benzene; 2.1 per cent AIBN on polymer; 220 per cent of theoretical amount of MeSH required to saturate; 50° C.

The rate of over 2 per cent addition per hour cannot be compared directly with any of the emulsion experiments because of the lack of correspondence in

concentration of initiator and mercaptan. However, it is of considerable significance that the rate is comparable in magnitude to those obtained in emulsion, in marked contradistinction to the difference in rates between emulsion and solution polymerization of, say, butadiene.

Soap coverage of the latex particles.—Kolthoff⁴⁰ was the first to show that the rate of emulsion polymerization of butadiene is affected by the extent to which the particle was covered with soap. Normal emulsion polymerization technology usually encompasses the range of 35 to 80–90 per cent saturation of surface. The greater the soap coverage, the higher the polymerization rate. To investigate this parameter in the mercaptan addition reaction a polybutadiene

TABLE II

Hours	% Saturation
3	6.9
5	13.5
22	49.5

latex, prepared to ca. 650 Å (surface average) was covered with soap to the following extents: 60 per cent, 75 per cent and 90 per cent. Under identical reaction conditions, these latexes did not differ significantly in the rate at which methyl mercaptan added to the polymer.

Efforts to derive overall rate expressions from various combinations of the equations developed by Sivertz and others³⁴ were not successful. A reasonably good representation of the experimental data was found with the empirical expression rate $dA/dt = k (RSH)(PB)^1$, where k is a proportionality constant.

In efforts to round out a picture of the role played by the several possible termination reactions, evidence was obtained on several occasions showing that the coupling of two polymer radicals, $2 A^* \rightarrow A_2$ (leading to a crosslink), can at most have only an insignificant part in terminating the kinetic chain. This is

TABLE III
VISCOSITY CHANGE DURING REACTION

% Saturation	Dilute solution viscosity	Osmotic \bar{M}_n
0	2.2	60,000
16	2.02	—
38	1.91	—
46.6	1.87	90,000
60	1.81	—
75	1.73	—
82	1.72	—

determined by following molecular weight changes during the addition reaction, which in general have been observed to keep pace with the change in saturation, and not to involve formation of such high molecular weight polymer as would be indicated by an appreciable crosslinking reaction. Typical data are shown in Table III.

The drop in viscosity is believed to be caused almost entirely by the change in the polymer-solvent interaction coefficient, μ , (solubility parameter), a point discussed in later section. Mooney plasticity measurements on a large number of runs have shown, on the average, that the reaction product of the addition reaction has the same Mooney as the starting material.

In attempts to measure analytically the possible termination reaction resulting from disulfide formation ($2 RS^* \rightarrow RSSR$), potentiometric titrations were

carried out on polybutadiene-methyl mercaptan reaction mixtures. Titrations on latexes where the residual mercaptan had been removed by stripping indicated traces of disulfide (<.02 per cent of the double bonds saturated). These latter results may not be conclusive, however, since the stringent conditions for removal of mercaptan were such as to make probable the removal of some or most of the disulfide.

The termination reaction involving coupling of a polymer and a mercaptyl radical, $RS' + A' \rightarrow RSA$, leads to formation of an alpha, beta substituted ethylene dithioether. Spectroscopic measurements have thus far been unable to detect any quantity of this structure in the polymer.

From the foregoing, the following generalizations may be made concerning the free radical addition of methyl mercaptan to polybutadiene:

(1) There is apparently not much similarity between the kinetics of mercaptan addition and kinetics of emulsion polymerization. This would be expected, if the inferences of Siverts and others' work²⁴ were also applicable here, namely, the chain transfer step ($A' + RSH \rightarrow AH + RS'$) is rapid and the attack reaction ($RS' + P \rightarrow A'$) is rate controlling. In contrast to "ideal" emulsion polymerization, apparently more than one radical can exist in a single latex particle for appreciable lengths of time (cf. high rates in solution), and the radicals are probably water soluble enough that they can diffuse out of the latex particles readily. The emulsion reaction may be formally analogous to a concentrated bulk reaction, the upper limit of mercaptan concentration being determined by the amount that can be sorbed into a latex particle.

(2) If polymerization reaction rates can be grouped into two classes—(1) those whose ratio of propagation to termination rate constants are comparatively low (e.g., butadiene), leading to very low rates in bulk compared to emulsion; and (2) those whose ratio of propagation to termination rate constants are comparatively high (e.g., styrene), leading to fairly high rates in bulk compared to emulsion—the methyl mercaptan addition to polybutadiene double bonds would probably be classed with the latter.

USE OF PHOTOCHEMICALLY INITIATED REACTIONS TO DETERMINE SOME OVERALL RATE CONSTANTS

The photochemically-initiated reactions were carried out in an attempt to characterize the kinetics of the reaction more precisely, and in particular to establish the role played by the various types of double bonds of the polymer in the overall reaction. After trial of a number of materials, benzoin was found to be an efficient photosensitizer for the reaction. The experimental results are shown in Figure 2.

It may be seen that an increase in the mercaptan charge from 100 per cent to 150 per cent of theoretical does not affect the overall reaction rate, whereas the rate was increased by an increase in the concentration of photosensitizer. The conversion versus time curve was analyzed on two assumptions; (1) that the rate of reaction was dependent upon the concentration of residual double bonds; (2) that the initiation and termination rate constants are comparatively unaffected by which type of double bonds are involved in the propagation (attack plus transfer) step, so that the latter constants might be determined, at least approximately, for each double bond type.

A first-order plot of the conversion versus time data could be resolved into three linear first order curves. These three plots apparently correspond to the rate

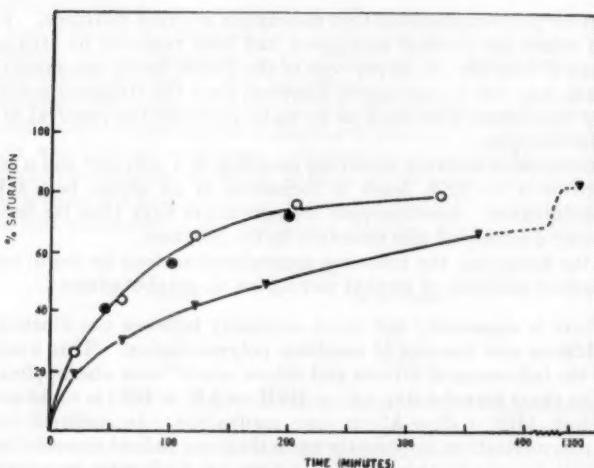


Fig. 2.—Addition of methyl mercaptan to polybutadiene in latex form
26.2% polymer; photochemical initiation

Benzoin, g/100 g polymer	Mole ratio, RSH/double bond
○ 0.96	1.0
● 0.96	1.5
▽ 0.32	1.0

of reaction of the three different types of double bonds present in the polymer molecule. The rate constants and relative initial concentration of three different types of double bonds are listed in the table below.

It must be pointed out that due to difficulty in resolving the overall conversion curve into three components, the above values can be considered approximate values only. From the relative concentrations of the different double bonds, they may be identified as probably resulting from 1,2, 1,4-*trans* and 1,4-*cis* addition (in order of decreasing reactivity towards methyl mercaptan). It is interesting to note that the considerable work on microstructure of polybutadiene and SBR carried out in the U. S. Government sponsored synthetic rubber program¹¹ pointed towards a probable ratio of 1,2:1,4-*trans*:1,4-*cis* of ca. 18:60:22.

INFRARED STUDIES OF THE PROGRESS OF THE REACTION

Figure 3 depicts the spectra of emulsion polybutadiene and of a 90 per cent saturated adduct of methyl mercaptan and polybutadiene over the range of 2

TABLE IV
RATE CONSTANTS FOR PHOTOCHEMICALLY INITIATED REACTIONS

Bond type	% of total double bonds	Calculated rate constants, k (hr^{-1})	
		0.32 g benzoin/ 100 g polymer	0.96 g benzoin/ 100 g polymer
a	15	2	3
b	55	0.3	0.8
c	30	0.03	0.07

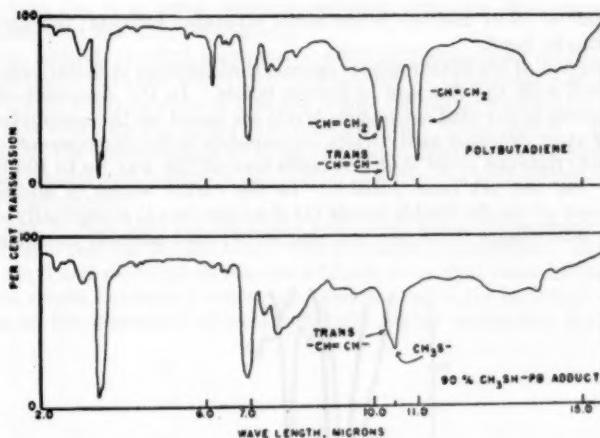


FIG. 3.—Infrared spectra of polybutadiene and a 90% saturated CH_3SH -PB adduct.

to 15 microns. In order to examine pertinent bands in more detail, portions of the spectrograms of thin films (calculated to be 0.08 mm) of polybutadiene and methyl mercaptan adducts between 10 and 11 microns (1000 and 910 cm^{-1}) are reproduced in Figure 4. In the region chosen, three bands characteristic of olefinic double bonds appear, two of them strong ones: at 10.37 microns from (*trans*) internal bonds and at 11.0 microns from the vinylic bonds. A weak

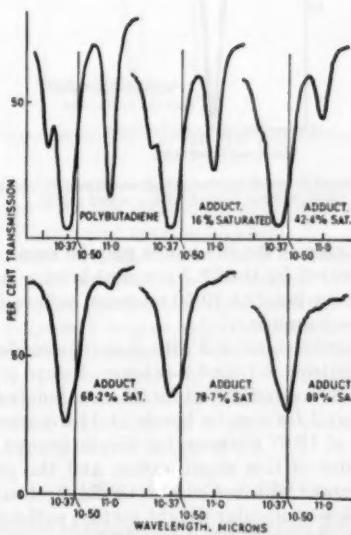


FIG. 4.—Infrared absorption spectra of a series of CH_3SH -PB elastomers having saturations from 0 to 90 per cent.

band appears at 10.07 microns in the lower saturated adducts; this also arises from the vinylic bond.

Examination of the spectrograms reveals that increase in sulfur uptake corresponds well with the decrease in double bonds. In the discussion that follows, references to per cent saturation levels are based on the assumption that each sulfur atom detected analytically corresponds to the disappearance of one double bond; rigorous proof that this holds true all the way up to 100 per cent saturation has not yet been possible. In the earlier stages of addition the disappearance of vinylic double bonds (11.0 micron band) is especially evident, and in the later stages (78.7 per cent and 89 per cent adduct) recession of the

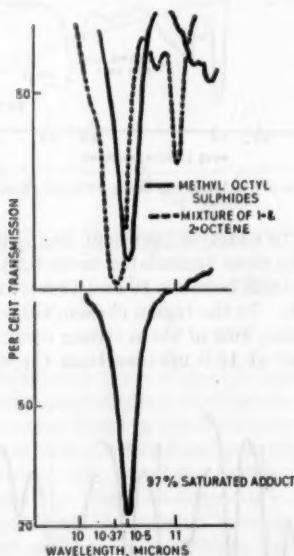


FIG. 5.—Comparison of infrared spectra of highest saturated methyl mercaptan—polybutadiene adduct with a model sulfide.

10.37 micron band for internal double bonds may be seen. The vinylic groups have essentially disappeared by the 78.7 per cent level. Also appearing in the later stages is a new strong band at 10.50 microns, believed to be characteristic of methyl thio- ($\text{CH}_3\text{S}-$) groups.

This spectrogram may be compared with those of a model compound, methyl octyl sulfide and the mixture of 1- and 2-octenes, Figure 5. The unsaturation of the octenes shows as (1) a strong band for internal bonds at 10.37 microns and (2) a relatively weak band for vinylic bonds at 11.0 microns. Also there is a trace of the weak band at 10.07 microns, for vinylic groups. The curve for the sulfide shows the absence of this unsaturation and the presence of the same strong band at 10.5 microns which occurs in the highest-saturated adduct rubber. Spectra of other low-molecular weight methyl sulfides are reported in the literature^{42,43}; all have strong bands near 10.5 microns. The above data, coupled with the fact that none of the adducts of polybutadiene with other

mercaptans has this band, indicate strongly that the 10.5 micron band is associated with the CH_2-S group.

When adducts of ethyl, isopropyl or *n*-propyl mercaptan with polybutadiene were compared with the methyl adducts having the same total degree of saturation, infrared analysis showed that the higher mercaptans saturated the vinylic bonds at a considerably higher rate than did methyl mercaptan. In Figure 6, portions of the spectrograms of films of similar thicknesses are superimposed, whereby methyl and isopropyl mercaptan adducts of about 45 per cent saturation are compared.

It may be seen that the isopropyl derivative has a considerably lower concentration of residual vinylic bonds than the methyl derivative. Spectrograms of the ethyl and *n*-propyl mercaptan adducts show that these mercaptans also saturate vinylic bonds at a rate comparable to that of the isopropyl mercaptan. Spectra of the isopropyl adducts with still higher saturation show that the

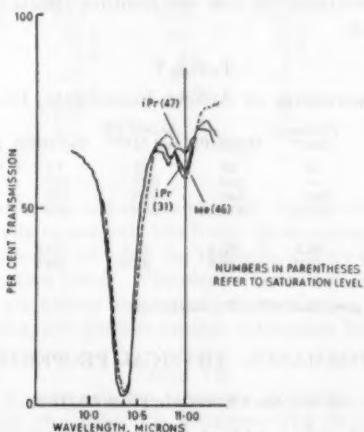


FIG. 6.—Portions of infrared spectra of MeSH and isopropyl SH adducts.

vinylic band at 11.0 microns has disappeared by 55 per cent total saturation. This may be compared with the methyl adducts, wherein the vinylic band has disappeared only by 78 per cent total saturation.

Conclusions from such data and from results of studies of oxygen absorption reported in a later section are that the free radical initiated reaction of polybutadiene with a mercaptan consists mainly of addition of the mercaptan to the double bonds of the polyolefin to give poly(thioether) structures. Other structures may be present in small amounts, e.g., the allylic sulfide grouping, $-\text{CH}=\text{CHCH}(\text{SCH}_3)\text{CH}_2-$, from attack of $\text{CH}_3\text{S}-$ groups on an alpha carbon atom; or the 1,2-*bis*(alkyl thioether) structure, $-\text{CH}_2\text{CH}(\text{SCH}_3)\text{CH}(\text{SCH}_3)\text{CH}_2-$, resulting from termination of a kinetic chain by a $\text{CH}_3\text{S}-$ group. These have not yet been detected in our work.

COMPOSITIONS STUDIED

All three of the major compositional parameters were studied in relation to properties to at least some degree: (1) type of base polymer; (2) extent of

saturation of the double bonds; (3) chain length and nature of mercaptan used for saturation.

Most of our effort has been directed to work on polymers and copolymers of emulsion polymerized butadiene; polymers of isoprene—both natural and synthetic—have also been used, as well as polychloroprene. Because performance in aging, solvent resistance, etc. improves as the extent of saturation increases, adducts of polymers whose double bonds have been at least 50 per cent saturated—and usually 70 per cent or more saturated—have commanded the most attention. In a like vein, research effort on the different alkyl mercaptans was somewhat in proportion to the attractiveness of their present or potential price structure; the low molecular weight mercaptans, especially methyl, merited the greatest attention in this respect.

Rather than report the performance data in terms of each compositional variable separately, it was deemed simpler to discuss the various properties separately, with observations on how composition affects each. This is done in the following section.

TABLE V
PHYSICAL PROPERTIES OF ADDUCT ELASTOMERS, GUM STOCKS

Elastomer	Fluoflex 1000*	MeSH-PB	MeSH-PB oil MB**	MeSH-PB	MeSH-PB	EtSH-PB
% saturation by RSH	0	46	46	75	90	70
300% modulus	—	250	225	136	110	140
Tensile, psi	210	340	250	470	590	260
Elongation, %	325	415	335	620	765	490
Vibrotester						
Dynamic modulus, kg/cm ²	39.2	37.4	19.7	31.3	31.3	24.2
Resilience, %	35.0	48.8	48.9	28.4	16.6	35.3

* "Hot" SBR.

** Masterbatch with 37.5 parts Shell SPX-97 extender oil.

PERFORMANCE—PHYSICAL PROPERTIES

GENERAL PHYSICAL PROPERTIES

The technology of using adduct elastomers—processing, compounding techniques, curing recipes, fabricating methods—follows very closely the methods conventionally used for the standard diene rubbers.

Handling properties appear to be indistinguishable from those of "hot" SBR; if anything, there appears to be a tendency for "smoother" extrusion, mill banding, etc. As further noted later in this section, cure recipes require little or no adjustment except for highly saturated adducts.

Some typical gum stock stress-strain and dynamic data at room temperature for mercaptan adducts of polybutadiene are compared with those of "hot" SBR in Table V. More complete room temperature physical data on tread-type stocks are given in Table VI. Except for a somewhat lower rebound, adduct elastomers appear to be quite similar to SBR in most of the usual physical properties. The features which distinguish them for special applications are discussed in later sections.

The ease of curing methyl mercaptan adducts of polybutadiene of increasing degrees of saturation in conventional gum stock recipes appears to be only slightly affected until a saturation level of approximately 85 per cent is reached. The swelling volume measurements listed in Table VII indicate that elastomers of this series in the range of 50 to 80 per cent saturated are somewhat more

readily cured than the base polybutadiene and much more easily cured than the adducts at the highest saturation levels.

In order to translate the swelling volume values directly into states of cure the solubility parameter, μ , for the elastomer at each saturation level would have to be known. Experience with these elastomers has shown that swelling volumes above 6 or 7 indicate relatively low states of cure. The 97 per cent saturated adduct at a swelling volume of 12 (60 minute cure) is still very lightly cured.

TABLE VI

PHYSICAL PROPERTIES OF ADDUCT ELASTOMERS, BLACK FILLED STOCKS

Elastomer	Phioflex 1000	Polybuta- diene*	MeSH-PB	MeSH-PB	MeSH-PB
% saturation by RSH	0	0	60	80	90
300% modulus	1270	1500	1670	1925	1200
Tensile, psi	2750	1750	2800	2750	2650
Elongation, %	530	330	480	430	630
Rebound—Goodyear	56.5	60	40.3	44.1	43.0
Ring abrasion, cc loss	3.6	2.6	2.8	3.4	5.8
Shore A hardness	57	63	66	66	64
Permanent set, %	3.3	4.0	1.1	1.4	3.5
SBR tear, cold	260	—	75	133	271
SBR tear, hot	120	—	20	41	215

* Base polymer for adducts.

In other cure rate studies not shown the very highly saturated adducts have been cured satisfactorily in activated or butyl-type curing systems.

As mentioned above the rebound (or resilience) of an adduct elastomer is a function of the saturation level. Vibrotester resilience values for gum stocks of methyl mercaptan adducts of polybutadiene, confirming the rather unpromising resilience properties, are plotted against saturation levels in Figure 7.

TABLE VII

THE EFFECT OF SATURATION LEVEL ON RATE OF CURE OF $\text{CH}_3\text{SH}-\text{PB}$ ADDUCTS—GUM STOCKS

Saturation, %	Swelling volume in benzene minutes cured at 300° F		
	20	40	60
0	5.4	5.6	5.3
34	6.2	6.3	5.7
47	5.5	5.3	5.2
67	5.1	4.8	4.4
76	5.4	5.1	5.2
86	5.3	5.1	5.6
93	6.1	5.9	5.6
97	24.	15.	12.

The dynamic modulus of an adduct elastomer is markedly influenced by the molecular weight of the mercaptan used in its preparation. Increasing the molecular weight of the added mercaptan—at least up to C_8 —decreases the dynamic modulus, in common with effects observed in lengthening the chain of substituent groups attached to other elastomeric polymers.

Over quite a wide range of saturation levels (ca. 40 to 75 per cent) the dynamic moduli of the cured gum stocks are nearly constant for each mercaptan. These values have been plotted against mercaptan chain length in Figure 8 up to amyl mercaptan.

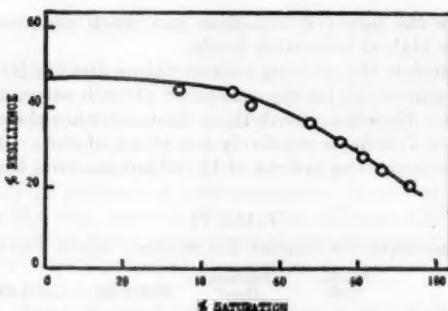


FIG. 7.—Effect of saturation level on resilience of CH_3SH -PB elastomers.

The dynamic moduli of the methyl derivatives (ca. 40–45 kg/cm^2) fall in about the same range as SBR; the propyl derivatives give moduli in the natural rubber range (ca. 25 kg/cm^2).

BASIC AGE RESISTANCE AND MECHANISM OF AIR AGING

Oxygen absorption measurements on methyl mercaptan adducts of varying saturation.—Oxygen absorption rate curves at 100° C of two series of well-purified methyl mercaptan-polybutadiene adducts covering a range of saturations are reproduced in Figure 9. The range extends from polybutadiene itself to adducts over 90 per cent saturated. On the graph the numbers indicate the per cent saturation.

The rate curves show that polybutadiene takes up seven per cent within a day, whereas methyl mercaptan-polybutadiene adducts absorb oxygen at drastically lower rates, the rate being inversely dependent on the extent of saturation.

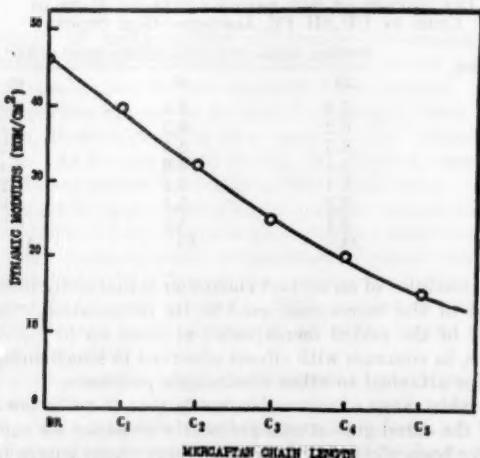


FIG. 8.—Effect of mercaptan chain length on dynamic modulus of PB adducts.

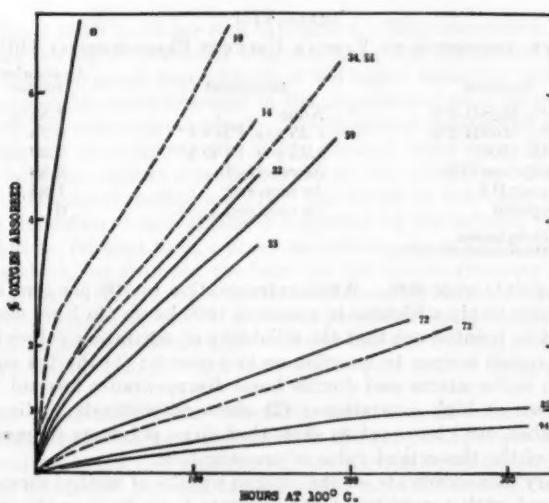


FIG. 9.—Rate of oxygen absorption by $\text{CH}_2\text{SH-PB}$ elastomers having various levels of saturation.
Numbers opposite curves give % saturation. O is unreacted PB.

A different treatment of the same data is shown in Figure 10, wherein the hours to 1 per cent absorption (log function) are plotted against per cent saturation. Again, a rather wide scatter persists up to 60 per cent saturation, but a saturation-independent region appears, followed by a sharp rise in hours to the higher-saturated region. The hours estimated for the 94 per cent saturated

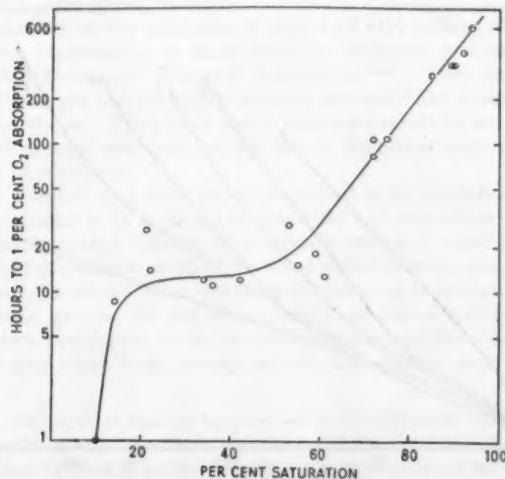


FIG. 10.—Relationship between hours to 1% absorption of oxygen
and % saturation of $\text{CH}_2\text{SH-PB}$ elastomers.

TABLE VIII
OXYGEN ABSORPTION BY VARIOUS UNCURED ELASTOMERS AT 110° C

Elastomer	Antioxidant	O ₂ absorbed, 100 hrs
92% MeSH-PB	None	1.86%
92% MeSH-PB	1.25 pts. PBNA*	0.75
SBR-1500	1.25 pts. PPDA**	1.30
Neoprene GN	As received	3.80
Hycar PA	As received	1.85
Hypalon	As received	0

* Phenyl-2-naphthylamine.

** A *p*-phenylenediamine derivative.

sample (last point) were 600. While extrapolation to 100 per cent saturation would seemingly imply a lifetime in excess of 1000 hours (to 1 per cent absorption), it must be pointed out that the reliability of saturation values in the 95-100 per cent region is open to question on two counts: (1) the 1:1 correspondence between sulfur atoms and double bond disappearance has not been conclusively shown at high saturations; (2) chemical methods (iodine number, bromine number, etc.) have yet to show that diene polymers themselves have 100 per cent of the theoretical value of unsaturation.

Preliminary measurements on the oxygen uptake of methyl mercaptan adducts stabilized with a variety of antioxidants have been confusing in that certain stocks have shown the evolution of gas instead of absorption. The properties of aged adduct stocks have shown that commercial rubber antioxidants, added in the amounts customarily used in SBR type polymers, effectively enhance the oxidation resistance of the adducts. A few typical absorption results on adducts and commercial elastomers are listed in Table VIII.

Oxygen absorption by ethyl, isopropyl and n-propyl mercaptan adducts of polybutadiene.—Figure 11 depicts the oxygen absorption rate at 100° C of purified adducts of polybutadiene and methyl, ethyl, isopropyl and *n*-propyl mercaptans,

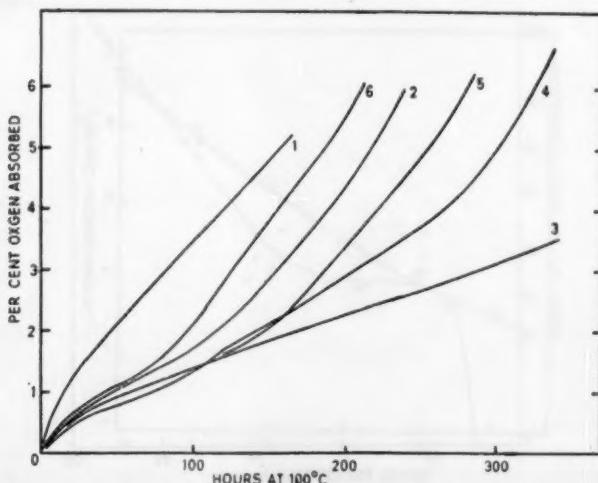


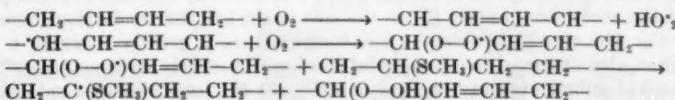
FIG. 11.—Effect of mercaptan structure on the rate of oxygen absorption of adduct elastomers: 1. CH₃SH-PB, 46% sat'd. 2. C₂H₅SH-PB, 41% sat'd. 3 and 4. i-C₃H₇SH-PB, 51 and 33% sat'd, respectively 5 and 6. n-C₄H₉SH-PB, 48 and 40% sat'd, respectively.

all in the range of 30 to 50 per cent saturation. The absorptions plotted take into account the higher molecular weight of the ethyl and propyl adducts. It is evident from the graph that adducts of the higher molecular weight mercaptans are appreciably more resistant in the unprotected state to oxygen attack than the methyl mercaptan adduct. The isopropyl mercaptan adduct is especially resistant in comparison with the methyl, since even the 32 per cent saturated isopropyl adduct absorbs oxygen at only about half the rate of the 45 per cent saturated methyl adduct. The cause of this difference between adducts of the different mercaptans is suggested by the infrared spectra of the various adducts, referred to in a previous section. In a 50 per cent saturated isopropyl adduct, for example, the band for the vinylic grouping (11.0 micron band) has almost disappeared, whereas in the corresponding 50 per cent saturated methyl adduct this band is still very prominent (and disappears only by about 70 to 75 per cent saturation). Hence the much lower concentration of the reactive vinylic groups in the isopropyl adduct confers the greater oxygen resistance.

Analysis of oxidized films.—Alcoholic extraction of some of the adduct rubber sheets which had been subjected to the action of oxygen at 100° C for several hundred hours and analysis of the extracts revealed the presence of amounts of a disulfide representing up to 2.6 mole per cent of the mercaptan originally incorporated into the adduct. In general, the higher the mercaptan saturation of the adduct, the lower the per cent disulfide which could be detected on oxidation. The amounts of disulfide detected ranged from 0.36 mole per cent for the 90 per cent saturated adduct to 2.6 mole per cent for the 34 per cent adduct. The moles of disulfide found per mole of oxygen absorbed varied from 0.03 for the 34 per cent saturated to 0.16 moles per mole of oxygen absorbed. An explanation for this phenomenon must await further work. Infrared analyses of films of the adducts demonstrated the development of carbonyl and sulfoxide groups after a few hours of aging. The hydroxyl band developed only after about 70 hours.

The mechanism of the oxidation of alkyl and aryl sulfides of various structures has been investigated in some detail by Bateman and coworkers of the British Rubber Producers' Research Association^{44,45}. They have studied the action of both oxygen and hydroperoxides on saturated and unsaturated sulfides in a variety of media. They have shown that the oxidations are complex, being composed of several reactions which occur simultaneously soon after the combination of reactants.

Since the disulfide and other products formed in the oxidation of the adduct polymers are similar to those found by Bateman and coworkers in the oxidation of allylic and saturated sulfides (the latter's oxidation needing certain free-radical catalysts), a similar series of reactions is presumed to occur in the adduct. In this instance, however, there are present saturated thioether structures plus isolated olefinic groups (in the incompletely saturated adduct). The most reactive centers would seem to be the olefinic bonds, but the attack on the thioether group may come from peroxy radicals first formed at *alpha*-methyleneic groups:



Degradation at the sulfide center would then follow Bateman's route.

The actual course of reaction in the polymeric adduct is further complicated by (1) the presence of olefinic groups in adducts which are less than 100 per cent saturated; (2) the relative immobility of the structures, sulfide, olefinic, etc., in the long polymer chains; (3) the possible presence of chain termination products from the original addition reactions, e.g.,



LOW TEMPERATURE FLEXIBILITY

Low temperature stiffening and embrittlement of adduct elastomers has been examined as a function of the extent of saturation, chain length of mercaptan, and composition of base polymer—the latter of which is treated in the fol-

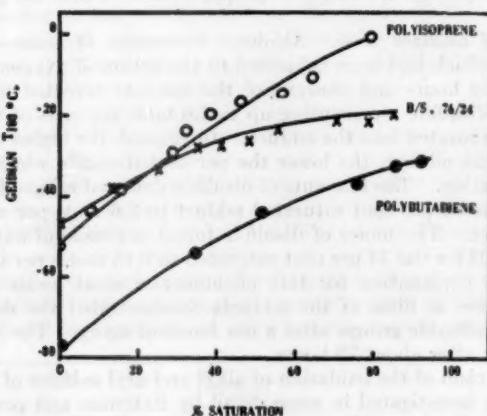
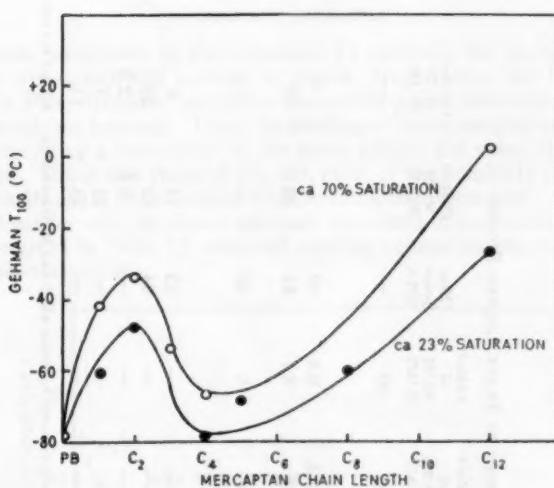


FIG. 12.—Effect of saturation level of MeSH-PB, MeSH-IR, and MeSH-SBR (76/24) adducts on Gehman T_{100} values.

lowing section on swelling properties. For adducts of the low molecular weight mercaptans and a particular base polymer, the glass transition temperature, T_g , rises as the saturation increases, the rate at which it rises being a characteristic of the base polymer. This property is shown by Figure 12 where Gehman T_{100} values (approximately equal to T_g) are plotted against saturation levels. The influence of mercaptan chain length on T_g is illustrated by the data plotted in Figure 13. Two levels of saturation are shown.

The unusual shapes of the latter curves are the consequence of several opposing influences: (1) for the lower mercaptans, the introduction of the polar sulfur atom at a high fraction of the double bonds detracts markedly from low temperature flexibility, an influence which is abetted by the ease of chain packing of the short side chains; (2) as the side chain lengths are further increased (C_8-C_6), the ease of packing at low temperatures is greatly lessened, a phenomenon also observed for the acrylate and methacrylate ester polymers⁴⁶ and for *p*-alkyl substituted styrene polymers⁴⁷; (3) for long aliphatic side chains (C_7 and up), the tendency of the latter to be immobilized into their own crystals

FIG. 13. Effect of mercaptan chain length on Gehmann T_{100} .

plays an important role in determining brittle temperature. No measurements for detecting actual crystallization have yet been run, however.

The similarity in the shapes of the curves at such widely differing saturations is itself quite noteworthy.

TABLE IX
SOLUBILITY PARAMETERS OF ADDUCT RUBBER

A. Properties of cured samples (gum stock)

Polymer	Swelling volume (vol/vol)	μ	Calculated M_s
65.5% sat'd PB/MeSH adduct Cure A	5.44	0.39	12,800
65.5% sat'd PB/MeSH adduct Cure B	5.34	0.39	10,900
89.5% sat'd PB/MeSH adduct Cure A	4.62	0.42	12,800
89.5% sat'd PB/MeSH adduct Cure B	3.79	0.42	7,100

B. Swelling volumes for 65.5% saturated PB/MeSH adduct

Solvent	Cure A		Cure B	
	Swelling volume	μ	Swelling volume	μ
Carbon tetrachloride	6.34	0.32	5.64	0.34
p-Xylene	5.20	0.35	4.62	0.34
75% Iso-octane, 25% toluene	1.05	0.73	—	—

C. Swelling volumes for 89.5% saturated PB/MeSH adduct

Solvent	Cure A		Cure B	
	Swelling volume	μ	Swelling volume	μ
Carbon tetrachloride	5.35	0.38	3.84	0.38
p-Xylene	4.47	0.40	3.26	0.39
75% Iso-octane, 25% toluene	0.66	0.85	0.60	0.85

TABLE X
SOLVENT RESISTANCE OF ADDUCTS OF VARIOUS BASE POLYMERS IN BLACK LOADED STOCKS

Polymer*	CH ₃ SH Saturation, %	Adduct of Poly B		Adduct of Poly B		Adduct of 90/10 B/AN		Adduct of 80/20 B/AN		Adduct of 65/35 B/AN		Neoprene GNA		Control 80/20 B/AN		Control 67/33 B/AN	
		Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B	Adduct of Poly B				
<i>% volume swell after 70 hours at 250° F</i>																	
Type A Auto Trans Oil	26	12	11	6.3	3.5	0.3	39	—	—	—	—	—	—	—	—	—	—
ASTM No. 3 Oil	57	39	39	25	18	8.7	81	38	38	38	38	38	38	38	38	38	18
<i>48 hours at room temp.</i>																	
Ref. Fuel B (standard mixture of aliphatics and aromatics)	41	36	35	32	36	19	49	—	—	—	—	—	—	—	—	—	—
<i>7 days at 77° F</i>																	
Iso-octane	—	7	—	3.7	—	—	—	—	—	—	—	—	—	—	—	—	—
70/30, Iso-octane/benzene	—	46	—	33	—	—	—	—	—	—	—	—	—	—	—	—	—
ASTM No. 3 Oil	—	4	—	2.9	—	—	—	—	—	—	—	—	—	—	—	—	—
Easo Turbo Oil No. 15	—	—	—	7.8	—	—	—	—	—	—	—	—	—	—	—	—	—
Kerosene	—	20	—	13	—	—	—	—	—	—	—	—	—	—	—	—	—

* Polymers contained 50 parts HAF or FEF black and were cured in conventional sulfur-accelerator recipes except neoprene which had MgO for curing. All had normal physical properties for the loadings used.

SOLVENT SWELLING

Solubility parameters in pure liquids.—To ascertain the change in solvent resistance associated with increase in degree of saturation (see following sections), the Flory-Huggins²⁹ solubility parameter μ was determined for several elastomer-solvent systems. From the swelling of cured samples in benzene and the corresponding μ determined in the same solvent the value of M_c could be calculated. Using this value of M_c , the value of the solubility parameter for other solvents could be calculated from swelling measurements. Two samples of adduct rubber were employed and each was cured to two levels of M_c . The values are given in Table IX where all swelling volume results are the average of two determinations.

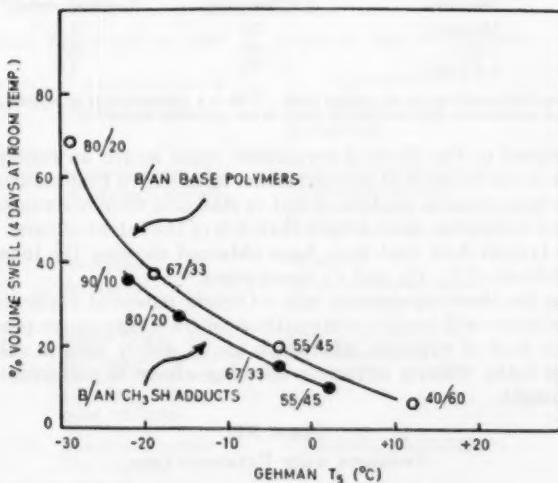


FIG. 14. Low temperature flex versus % swell in 70/30, isoctane/toluene.

The swelling volumes for the two types of adduct and the calculated μ values are also given in Table IX. It may be seen that an increase in the degree of saturation produces a small but significant increase in the solubility parameter, confirming the increased solvent resistance at the higher saturation level.

Solvent resistance in oils and fuels.—Addition of methyl mercaptan produces elastomers having considerably better solvent resistance than the base polymers, the solvent resistance increasing with saturation as shown in Table X. Above approximately 50 per cent saturation, the adducts of polybutadiene are more resistant to many oils and fuels of practical interest than is neoprene under similar conditions. The 80 to 90 per cent saturated adducts approach commercial types of 80/20 butadiene/acrylonitrile (B/AN) copolymers. To attain greater solvent resistance, adducts of appropriately chosen B/AN base polymers make possible nearly any desired degree of solvent resistance. The 78 per cent saturated adduct of 90/10 B/AN copolymer has solvent resistance characteristics intermediate between those of the unadducted 80/20 and 67/33 B/AN copolymers.

Data are presented in graphical form in Figure 14 which illustrate how sol-

vent resistant polymers with improved low temperature flex properties may be prepared. The Gehman low temperature flex values of B/AN and adducts of B/AN copolymers at various B/AN ratios are plotted against volume swell in a commonly used reference fuel. These results, along with those given in Table X, indicate that an 80/20 B/AN copolymer 80 per cent saturated with methyl mercaptan has a solvent resistance equal to the 67/33 unaducted copolymer and is flexible at a temperature at least as low as the latter. An added advantage is the increased high temperature stability of the adducted polymer.

TABLE XI
DEPENDENCE OF VOLUME SWELL ON MERCAPTAN CHAIN LENGTH

Mercaptan	% Saturation	Volume swell in fuel-type mixture*
Methyl	76	2.4
Ethyl	70	3.2
n-Propyl	73	3.4

* In cc of swollen sample per cc of original stock. This is a different basis of reporting than the "% Swell" figures of end-product type compounds given in the preceding section.

With respect to the effect of mercaptan chain length on swelling in fuels, evaluations of the adducts of polybutadiene have shown that volume swell in a 70/30 iso-octane/toluene mixture of fuel (a standard reference mixture) is more a function of mercaptan chain length than it is of the extent of cure. The table below lists typical data that have been obtained showing the increased swell with the adducts of C₁, C₂, and C₃ mercaptans.

Capacity for absorbing extender oils.—Certain potential applications of the adduct elastomers will involve compositions where it may prove possible to use the common type of extender oils, which are so widely used in cold SBR, to attain lower costs, without adversely affecting whatever performance features are being sought.

TABLE XII
SWELLING WITH EXTENDER OILS

Commercial name of oil	% Aromatic content*	Cc oil/cc elastomer sorbed into pre-cured:	Adduct of PB/MeSH	Plioflex 1502**
Necton 60 (Enjay)	21	0.16	1.22	
Circosol 2-XH (Sun)	44	0.39	1.60	
SPX-97 (Shell)	69	1.06	2.34	
Cauliflux GP (Golden Bear)	75	1.30	2.44	
Dutrex 20 (Shell)	93	1.51	2.38	
Benzene		4.38	5.63	

* As estimated roughly by silica gel method. The various oil manufacturers' methods for rating aromatic content are not always in concordance. Hence these values are only approximate.

** Cold SBR.

In order to gain some notion of the capacity of the cured stocks to "hold" oil without bleeding, a number of typical extender oils—covering a wide range of aromatic oil content—were used as swelling agents for a 70 per cent saturated methyl mercaptan-polybutadiene adduct which had been fully cured in a standard sulfur-type recipe. Table XII summarizes the data, in which the swelling of a hydrocarbon rubber (cold 50 ML SBR) are included for comparison. It is quite evident that the less aromatic oils cannot be used at the customary concentration levels (25–50 parts/100 of rubber) in the case of the adduct poly-

mer. The difference in sorption capacity between the adduct elastomer and Plioform 1502 decreases as the aromatic content of the oil increases.

PROPERTIES AND AGE RESISTANCE AT HIGH TEMPERATURES

Preliminary screening tests were made on a few of the more heat resistant rubbers, both as raw elastomers and as cured gum stocks, to evaluate their stability at high temperatures.

Table XIII summarizes observations made on the raw elastomers. The adduct rubbers contained 1.25 per cent of a nonstaining phenolic antioxidant—i.e., were not stabilized for maximum heat resistance. The other elastomers

TABLE XIII
HIGH TEMPERATURE (500° F) AGING OF RAW ELASTOMERS

Elastomer	Appearance after 1 hr	Appearance after 4 hrs	Weight loss*
Kel F-214	Slight darkening	Light brown color throughout	0.4%
CH ₃ SH-Adducts 97% Sat. PB	Darkened thin skin on exposed surface	Thin black resinous skin on exposed surface. Interior appeared unchanged. Some distortion of sample	3.4
90% Sat. PB	As above	As above	3.6
Hycar A-21	As above	As above except some bubble formation	6.4
Viton A	Black melted surface, spongy, expanded to about 5 times original volume. Strong acidic odor while hot	Very little change on further aging	1.2
Neoprene GN	Black and brittle like charcoal	No significant change after 1 hour	12.8
Hypalon	Dark brown blown sponge, several times original volume. Considerable decomposition	Not much change in appearance, but much more brittle	19.3

* Corrected for moisture content as determined by 2 hours heating at 220° F under 28 inches of vacuum.

were used as received. Earlier aging tests at 300° F had shown such rapid deterioration of conventional diene rubbers (SBR, natural rubber), even when protected with "strong" antioxidants, that these were not included in the 500° F tests. On the basis of appearance Kel F-214, a fluoroelastomer, was the least affected by 4 hours aging at 500° F.

It is not known how significant are the figures on apparent weight loss, since there may have been concurrent formation of nonvolatile oxidation products.

In further work, tread-type formulations have been tested as well as aged at high temperature. Table XIV lists the first results obtained at 400 and 500° F. The highly saturated adduct polymers appear to possess and retain the best balance of tensile and elongation values found in this series of elastomers. It

is believed that even further improvement in high temperature aging will be realized as more is learned about its basic aging properties.

OZONE RESISTANCE

Highly saturated methyl mercaptan adducts of polybutadiene have proven to have outstanding resistance to degradation when exposed to ozone at 100°F under both static and dynamic conditions. The 90 and 97 per cent saturated adducts, as well as butyl rubber, with no added protective agents (other than antioxidants included in the preparation of the raw polymers) showed no degradation after a total exposure including 200 hours at 50 parts per hundred million, 24 hours at 2000 pphm and 24 hours at 2750 pphm of ozone. Next in resistance were the 82 per cent saturated adduct and Neoprene GN which

TABLE XIV
HIGH TEMPERATURE PROPERTIES OF BLACK LOADED STOCKS *

Elastomer (% values are degrees of saturation)	Tensile, psi/Elongation, %			
	Original measured at			Aged 2 hrs @ 400°F
	77°F	400°F	500°F	77°F
88% CH ₃ SH-PB	2785/550	490/285	310/185	2000/255
90% CH ₃ SH-PB	1770/715	420/315	210/220	1900/460
Philprene VP-A	3190/445	480/200	146/23	890/190
Viton A	1440/200	—	270/90	—
Acrylon EA-5	1890/245	410/105	290/100	1960/115**
Acrylon EA-5***	1875/480	580/160	340/110	—
Natural rubber***	3850/480	500/500	20/10	—
Neoprene***	3550/480	770/100	215/10	—

* Adducts and Philprene VP-A stocks contained 50 parts ISAF black; Viton A, 20 parts MT (as recommended by du Pont); Acrylon EA-5 and natural rubber, 50 parts HAF; and neoprene, 50 parts MPC. Cure recipes were those recommended for maximum heat aging.

** Aged 90 hours at 300°F which our experience has shown to be about equivalent to 2 hours at 400°F.

*** Data from WADC Technical Report 56-331.

appear to have about equal resistance to ozone degradation (no visible degradation under static conditions for the exposure mentioned above but some cracking in the flexed samples after 200 hours at 50 pph plus 24 hours at 2000 pphm). The 69 per cent saturated adduct without added antiozonant appears to be approximately on a par with Plioflex 1710 (Oil extended cold SBR) containing an effective antiozonant.

GAS PERMEABILITY

In studies of the gas permeability of various elastomers van Amerongen⁴⁸ concluded that (1) low level of unsaturation, (2) high concentration of methyl groups (many short branches) and (3) polar groups were all conducive to low gas permeability of an elastomer. The highly saturated methyl mercaptan adducts of polybutadiene should therefore approach the ideal in this characteristic. Hydrogen and air permeability values for various adduct stocks as well as for several commercial elastomers are listed in Table XV. These results show (1) an inverse relation between extent of saturation and permeability; (2) that the best adduct gum stocks have about four and five times the resistance to hydrogen permeability shown by polybutadiene and natural rubber,

TABLE XV

HYDROGEN AND AIR PERMEABILITY OF ELASTOMERS AT ROOM TEMPERATURE

Elastomer	Type of stock	Hydrogen permeability, l/m ² /24 hr/0.001 in.
Butyl*	Gum	14
97% CH ₃ SH-PB adduct	Gum	27
82% CH ₃ SH-PB adduct	Gum	30
69% CH ₃ SH-PB adduct	Gum	34
Polybutadiene	Gum	109**
Natural rubber	Gum	127**
Butyl	30 parts MPC	3.9-10.7
97% CH ₃ SH-PB	50 parts HAF	4.9
90% CH ₃ SH-PB	60 parts HAF	3.1-6.0
		Air loss
Natural rubber	Carcass	1 (Arbitrary Unit)
Blend, 75/25, NR/77% CH ₃ SH-PB	Carcass	0.70
Blend, 50/50, NR/77% CH ₃ SH-PB	Carcass	0.45
Blend, 25/75, NR/77% CH ₃ SH-PB	Carcass	0.24
77% CH ₃ SH-PB	Carcass	0.16
Butyl	Tube	0.15

* Van Amerongen⁴⁴ reports 18.7 at 25° C.** From van Amerongen⁴⁴.

respectively, and about half that of butyl. In black stocks, which are of much more practical interest, the highly saturated methyl mercaptan adducts of polybutadiene are equivalent to butyl. A range of values is given in some instances where different batches of the same stock have been tested. Similar excellent performance for the adducts is also found for air permeability in black stocks.

EXPOSURE TO GAMMA RADIATION

Resistance to deterioration of vulcanized compounds.—Eighty-nine per cent saturated methyl mercaptan polybutadiene adduct, neoprene, and natural rubber in conventional reinforced stocks of the type used in commercial products,

TABLE XVI
EFFECT OF GAMMA RADIATION ON CURED BLACK STOCKS

Elastomer	Adduct*	Neoprene GN	Natural rubber
Total pigment	55 parts	26 parts	33 parts
Tensile, psi			
Original	1800	2900	3650
After 0.05 × 10 ⁶ REPs	1925	2650	2975
After 1.0 × 10 ⁶ REPs	2550	500	625
Elong. at break, %			
Original	580	900	605
After 0.05 × 10 ⁶ REPs	550	835	525
After 1.0 × 10 ⁶ REPs	350	120	140
300% modulus, psi			
Original	1000	350	950
After 0.05 × 10 ⁶ REPs	1150	375	1000
After 1.0 × 10 ⁶ REPs	2325	—	—

* 89% saturated methyl mercaptan adduct of polybutadiene.

were compared for their ability to resist degradation when exposed to radiation (gamma rays) from a Cobalt 60 source.

The results given in Table XVI show the serious deleterious effect on the neoprene and natural rubber stocks at an exposure of 10^8 REPs in line with the results reported by the Goodrich group³¹. The increase in tensile (probably due simply to further crosslinking) with a retention of over 60 per cent of its original elongation by the adduct elastomer under the same conditions indicates high resistance to degradation by gamma radiation.

Inasmuch as natural rubber itself has been rated by the Goodrich studies³¹ as one of the elastomers most resistant to gamma radiation, the performance of the stock based on adduct rubber make the latter class of elastomers look extremely promising from the standpoint of the many critical rubber uses involving radiation exposure.

Gamma radiation as a means of curing.—Methyl mercaptan adducts of polybutadiene at saturation levels from 0 to 97 per cent were irradiated for varying exposure times. Swelling volume measurements on these samples, listed in Table XVII show that considerably fewer crosslinks are formed in the highly

TABLE XVII
THE EFFECT OF GAMMA RADIATION ON RAW $\text{CH}_3\text{SH-PB}$ ELASTOMERS
OVER A RANGE OF SATURATION LEVELS

Saturation, %	Swelling volume in benzene after exposure to		
	2×10^7 REPs	4.5×10^7 REPs	6×10^7 REPs
0	7.3	5.5	4.8
34	8.5	5.6	4.7
47	8.5	5.6	4.7
67	8.5	5.9	4.7
76	7.7	5.9	4.9
86	9.8	6.2	5.5
93	13.9	9.5	7.0
97	15.2	9.9	8.1

saturated elastomers. These results indicate that a 97 per cent saturated adduct, prepared in a compounded stock, should give even better resistance to degradation than that observed above with the 89 per cent saturated material.

COMPATIBILITY OF ADDUCT ELASTOMERS WITH NATURAL RUBBER AND PLIOFLEX 1502

The effect of saturation level and molecular weight of the mercaptan on compatibility of adducts with natural rubber and Plioflex 1502 was examined by Dobry's solution separation technique³². The results indicate that the compatibility of adducts of polybutadiene with the hydrocarbon elastomers (1) decreases with increasing saturation, (2) increases with increased molecular weight of the mercaptan at equivalent saturation levels and (3) the methyl and ethyl adducts are more compatible with Plioflex 1502 (cold 50 ML SBR), while the higher molecular weight mercaptan adducts are more compatible with natural rubber. Methyl mercaptan adducts of butadiene/styrene elastomers show only slightly more compatibility than similar adducts of polybutadiene. The methyl mercaptan adduct of polyisoprene is similar to its polybutadiene counterpart in being more compatible with Plioflex 1502 than natural rubbers.

It should be pointed out that the "apparent" macrocompatibility of the adduct elastomers as judged by the ease of blending them with other rubbers on

a mill is seemingly high for SBR, Hevea, nitrile rubbers, and other commercial materials. These compatibility data are a useful forewarning of trouble that may be encountered in adhering adduct elastomers to dissimilar rubbers, or in certain properties of stocks prepared from blends of the elastomers.

TYPICAL END USE APPLICATIONS

The very wide range of performance properties available in the adduct elastomers make them very attractive candidates for replacing or supplementing presently available "specialty" rubbers in a large variety of end products. Cited below are four representative cases of products where MeSH-PB adducts have offered promise of doing a job as well or better than has been possible by rubbers already in use:

Separately mountable white or colored sidewalls for tires.—Since black tire sidewalls are usually compounded with dark staining oils which tend to diffuse through the demountable type white walls, developing a satisfactory compound which is resistant to this stain transfer has been a major technical problem. By virtue of their resistance to diffusion to both large and small molecules, the adduct elastomers are well suited for use as partial replacements for the hydrocarbon rubbers usually employed. Blends of 30 per cent adduct (MeSH-PB, 75% saturated) with natural rubber in white pigmented stocks have shown greatly improved resistance to the transfer of stain when placed on staining tire compounds and tested in a weatherometer as well as under actual exposure conditions.

Radiator coolant hose.—There are many automotive applications where a performance specification has been slowly evolved which tends to favor the use of a particular type of rubber. Radiator cooling hose, for example, is made in a number of grades, and one of these, SAE Specification 20R1, Class SC, is built around neoprene. Inasmuch as the polybutadiene-methyl mercaptan adducts have, in general, greater solvent resistance than neoprene, advantage was taken of this property to use blends of adduct rubber with a hydrocarbon rubber to build a compound which would adequately serve the application. Blends, containing from 75 to 200 parts of adduct per 100 parts hydrocarbon rubber and compounded with 60 parts black on total polymer, were found satisfactory to meet the specification mentioned above.

Impregnant for airship fabric.—Major performance requirements for rubbers used in coating airship fabrics are diffusion resistance and age resistance. Nylon fabric coated with a 90 per cent saturated MeSH-PB adduct elastomer has withstood aging tests well to date, although the tests have not yet been running long enough to determine how the fabric's lifetime would compare with neoprene-coated nylon.

The lower density of the adduct polymer (approx. 1.07) gives it a considerable weight advantage over neoprene (density 1.25) in an application where weight savings are all important. Incidentally, the reason butyl rubber is unsuited for this application is that the seams are cemented together with air curing cements.

Oil resistant foam for railroad journal boxes.—A major new use for oil resistant foam which is now looming is the introduction of foam rubber in place of wads of cotton to "hold" lubricating oil in place in railroad car journal boxes. Oil resistance, heat resistance, and retention of shape are the necessary properties for this application. A conventionally prepared foam rubber sample, made from a 62 per cent solids MeSH-PB adduct latex, has looked very promising in

comparison with neoprene in tests which are being set up to screen rubber foams for this application.

STATUS OF COMMERCIAL DEVELOPMENT

Recent introduction of the alcohol-hydrogen sulfide process for making mercaptans in the U. S. has enabled certain of the lower members to be offered at prices in the same range as many of the large volume monomers used for making presently available commercial rubbers. The manufacture of adduct elastomers, although somewhat similar in technology and equipment to that used for making SBR and like polymers, is sufficiently different to require substantial alterations in plant installations. The long range prospects for manufacture of many types of this versatile new family of elastomers at prices competitive with present high performance rubbers are considered very encouraging.

Our preparation experience with adduct rubbers has been carried into an advanced pilot plant stage, mostly on derivatives of methyl mercaptan. All polymer has so far been consumed in fabricating operations within our own company. The rubbers are not as yet being made in sufficient volume to be offered for outside sale or for sampling.

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SUMMARY

A versatile family of elastomers has been prepared by free radical addition of aliphatic mercaptans to the double bonds of diene polymers. High saturation levels were readily achieved without degradation of the basic polymer chain. The technology is similar to ordinary emulsion polymerization.

By varying the nature of the base polymer, the mercaptan used, and the extent of saturation, a wide range of compositions and of physical properties were attained in the adducts. In general, resistance to aging, ozone attack, heat, solvent swelling, and to permeation by gases increased with increasing extent of saturation. Outstanding performance in these qualities was achieved by adducts of polymers whose double bonds had been over 90 per cent saturated. A highly saturated methyl mercaptan adduct of polybutadiene showed (1) stress-strain and air aging properties at 400° and 500° F better than commercially available ethylacrylate copolymers and various semicommercial heat resistant elastomers; (2) permeability resistance equivalent to butyl; (3) solvent swell intermediate between neoprene and medium nitrile content butadiene-acrylonitrile rubbers, with a T_g below -30° C; (4) ozone resistance comparable to the better commercially available saturated rubbers. Increased solvent resistance was obtained by preparing adducts of the appropriate butadiene-acrylonitrile copolymers.

Adducts with saturation levels up to about 85 per cent could be cured by the same procedures used for the base polymers. Activated or butyl-type curing systems were required for higher saturation levels.

The relative rates at which aliphatic mercaptans add to the several types of double bonds present in emulsion diene polymers have been examined in a preliminary way.

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THE MUTUAL SOLUBILITY OF POLYMERS. II. THE VISCOSITY OF MIXED RUBBERS AND THE BEHAVIOR OF SOLUTIONS OF THESE *

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In the previous paper¹ an opinion, based on the physicomechanical properties of vulcanizates, was advanced as to the mutual insolubility of SKB (polybutadiene) and SKS-30 (butadiene-styrene) rubbers under the conditions characteristic of vulcanize formation. In order to clarify this question further, the viscosity of uncured rubber stocks composed of a combination of these rubbers was studied, along with the general properties of mixtures of solutions of different rubbers.

The viscosity of uncured rubber stocks.—The viscosity of polymers, including raw rubber stocks, can be determined by measuring the true residual (irreversible) deformation (i.e., the permanent set) produced by the action of a given stress². At a sufficiently high temperature, where a steady flow is achieved quickly, and for stresses and deformations which are not very great, one may use the following simple approximate equation³ for the calculation of the viscosity:

$$\sigma = \eta \frac{d\epsilon}{dt}$$

where σ is the stress, ϵ the permanent elongation or compression set, t is time and η is the viscosity.

We carried out the viscosity measurement by the use of a dynamometric balance⁴ with monoaxial compression stress (the temperature being kept in the range of 98–100° C during the measurements). Since the stress during the deformation remained practically constant in our experiments (the displacement being small in comparison with the thickness of the sample), the viscosity could be estimated from the equation:

$$\eta = \frac{\sigma t}{\epsilon}$$

Figures 1 and 2 give data obtained by this method on the viscosity of rubbers, mixtures of rubbers, and raw rubber stocks prepared from a base of a combination of rubbers.

As the figures show, some systems (SKB + natural rubber, SKS-10 + SKS-30) exhibit no peculiarities at all. In these systems the viscosity changes only gradually with a change in the proportions of the mixed rubbers. The systems SKS-30 + SKB and SKS-30 + natural rubber, however, differ substantially from the others in that the mixing of rubbers in these cases causes a

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from *Zhurnal Fizicheskoi Khimii* 30, 8, 1746–1751 (1956).

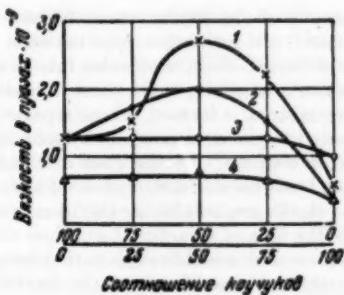


FIG. 1.—Viscosity of (dry) mixtures of two rubbers. 1—SKS-30 + SKB; 2—SKS-30 + natural rubber; 3—SKS-30 + SKS-10; 4—SKB + natural rubber. The abscissa represents the proportions of the rubbers in per cent, the ordinate the viscosity in poises $\times 10^{-3}$.

considerable rise in viscosity. Thus this study of the fluidity of combined rubbers confirms the conclusion which we drew earlier¹ from the study of properties of combined stocks, in regard to the anomalous properties of some polymer mixtures, and particularly those of mixtures of SKS-30 with SKB and with natural rubber.

If we accept the basic assumption that the process of mixing two rubbers is a process of mutual solution of two liquid phases, then we must conclude that the appearance of the maximum, on the curve of viscosity versus proportions of the rubbers, indicates something other than a simple mixing of two kinds of molecules. There are two possible reasons for a rise in viscosity in mixed poly-

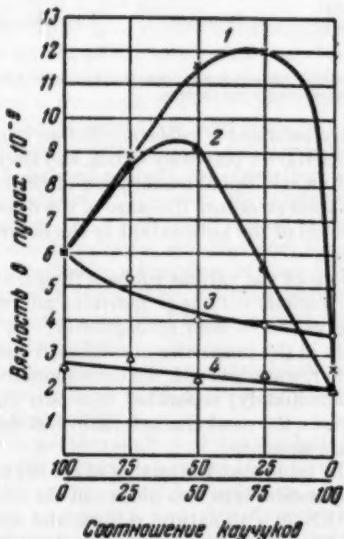


FIG. 2.—Viscosity of raw rubber stocks prepared from a base of two rubbers combined. 1—SKS-30 + SKB; 2—SKS-30 + natural rubber; 3—SKS-30 + SKS-10; 4—SKB + natural rubber. The abscissa represents the proportions of the rubbers in per cent, the ordinate the viscosity in poises $\times 10^{-3}$.

mers. Firstly, the viscosity of the mixture may become greater than that of either component polymer if a reaction develops between the mixed molecules, such as would link the different chain molecules into a more complex spatial structure. Secondly, a rise in viscosity takes place if, instead of a homogeneous stock, a microhomogeneous stock is formed, whose separate regions (of different composition) are connected together as a whole by long chain molecules which pass through several such regions. In the case of the mixed rubbers under consideration, there is no basis for any assumption of a strong reaction between chains. Further, these stocks are soluble in the usual rubber solvents, which fact directly contradicts the idea of structure formation through intermolecular reaction. Thus only the second possible explanation remains—the micro-non-homogeneity of the mixed stock, resulting from the limited mutual solubility of the rubbers.

In this connection, it is important to study the behavior of mixtures of solutions of rubbers.

TABLE I
CHARACTERISTICS OF MIXTURES OF 5% SOLUTIONS OF RUBBERS
(Ratio of solution volumes, 1:1)

Rubbers*	Solvent	Characteristic behavior of solutions
SKS-30 + SKB SKS-30 + natural rubber }	Gasoline	Two phases separate
SKS-30 + SKS-10 SKB + natural rubber }	Gasoline	They remain homogeneous
SKN-18 + SKB SKN-18 + SKS-30 SKN-18 + natural rubber }	Benzene	Two phases separate

* Translator's Note: SKB is a sodium-catalyzed polybutadiene rubber, SKN a butadiene-nitrile rubber, and SKS-10 and SKS-30 are butadiene-styrene rubbers.

The behavior of mixed solutions of rubbers.—Before being dissolved the rubbers were plasticized to a Karrer plasticity of 0.5, and they were then dissolved. It should be noted that an additional purification of the rubbers usually causes a substantial change in their structure (because of the development of oxidation reactions after the removal of the antioxidant in the course of purification) and is therefore not desirable.

Five per cent solutions of the various rubbers (based on the total amount of solvent) were mixed in various volume proportions and were studied from the standpoint of the preservation of their homogeneity. It was found that in all cases where the anomaly in the properties of combined cured or uncured stocks, which we described earlier, was observed, the corresponding solutions after some time (or sometimes immediately) separated into two distinct phases; this is indicated by Table I, where the most characteristic systems which did or did not separate into phases⁷ are presented.

It is evident from the table that the mixing of rubber solutions of equal concentrations causes a separation into two phases in the case of mixing solutions of SKS-30 with SKB, SKS-30 with natural rubber, and also SKN-18 with SKB, SKS-30 or natural rubber. However, mixtures of solutions of SKS-30 with SKS-10 and of SKB with natural rubber remain homogeneous, even for four years after the mixing.

The mixing of different volumes of rubber solutions equal in concentration introduced nothing substantially new into the phase separation situation. Thus, for example, mixtures of solutions of SKS-30 and SKB in different volume ratios of the components (from 10 to 90% by volume) separated into two phases in a period of one day.

A study of the effect of concentrations of the mixed rubber solutions on their separation, made with mixtures of SKB and SKS-30 solutions in gasoline, proved more interesting, however. Solutions of equal concentration were mixed together in equal volumes. The concentrations studied were 1, 2, 3, 5 and 10% by weight.

It was found that with concentrations in excess of 1% the solutions separated into two phases. One % solutions did not separate, however, but remained homogeneous for a long time. It was of interest to discover whether or not this critical concentration of the mixed rubber solutions depended on the nature of the solvent. Preliminary experiments which were carried out on mixed solutions of these same rubbers in benzene, however, showed that the separation into phases begins at a somewhat higher concentration. Since separation into phases is a direct result of interaction between molecules of the different rubbers in solution, it is plain that with a sufficiently great dilution, where collisions between molecules of one rubber and those of another occur hardly at all, any rubbers (and any polymers in general) may coexist in solution without their separating into phases, provided only that they are soluble in the given solvent. Hence it is quite natural that with a change in the solvent, the critical concentration (below which the solutions remain homogeneous but above which they separate into phases) changes also; since the elasticity of the chain molecules, and consequently their sizes, depend essentially on the surrounding medium, i.e., on the nature of the solvent.

A separation of the mixtures of rubber solutions into two phases shows that the heat effect of the mixing of the solutions in question is negative, i.e., that the mixing of solutions in these cases takes place with an absorption of heat. It is quite evident that if the chain molecules are sufficiently elastic, the heat effect of mixing such rubbers apart from their solvents will likewise be negative.

In the case of mixing polar with nonpolar rubbers (SKN-18 + SKB, SKN-18 + SKS-30, SKN-18 + natural rubber), the correctness of the conclusion drawn earlier is beyond any doubt. However, the systems SKS-30 + SKB and SKS-30 + natural rubber, in which both mixed rubbers are nonpolar, also separate into two phases in solution, and therefore the mixing of rubber solutions in these cases undoubtedly takes place with an absorption of heat. This conclusion agrees fully with the well-known endothermic nature of a mixing of low molecular weight liquid saturated hydrocarbons with aromatic hydrocarbons (e.g., octane with benzene).

It is strange, however, that while an anomaly in mechanical properties is exhibited in the system SKS-30 + SKB, no such anomaly is observed in the system SKS-30 + natural rubber¹.

Since we have made no thorough study of the latter system, we may only conjecture that the polar impurities present in natural rubber, which play no substantial part in the mixing of rubber solutions of low concentration are, nevertheless, sufficient to prevent any stratification in the system SKS-30 + natural rubber in vulcanization. It would thus undoubtedly be of interest to study the mechanical properties of vulcanizates of mixed SKS-30 and natural rubber, prepared from natural rubber purified of polar impurities and from

ordinary SKS-30. Probably in this case the system SKS-30 + natural rubber would prove to be analogous to the system SKS-30 + SKB⁵.

The data obtained on the behavior of mixtures of solutions of rubbers with equal concentrations show that in all cases where the combined stocks or mixtures of rubbers possess anomalous properties, the corresponding solutions of the rubbers separate into two phases. Thus the opinion which we expressed earlier¹, that these anomalies are related to the mutual insolubility of the rubbers, is confirmed by the behavior of mixed solutions.

Further, a study of mixtures of solutions also shows that any attempt to explain the anomalies in mechanical properties which have been observed in some combined stocks on the basis of a supposed chemical reaction between the mixed rubbers should be rejected if only because both the phases formed are fully soluble in excess solvent, and the process of separation of the solution into phases is reversible and in equilibrium. Thus not only the complex of mechanical properties of the combined stocks, but also the behavior of mixed solutions of the rubbers, lead to the conclusion that the mutual solubility of polymers is highly limited, and that consequently the majority of such mixtures will have a micro-nonhomogeneous structure unless special measures are taken to prevent it.

In this connection it is of interest to clarify the reason for the reduced mutual solubility of polymers as compared with their low molecular weight homologues and with polymer-solvent systems.

It is known that the entropy of mixing of two low molecular weight liquids is so considerable that many of these are miscible at room temperature, in spite of the absorption of heat (for example, benzene and octane). In the case of mixing a polymer with a low molecular weight liquid, instances are also known of an endothermic infinite solubility (e.g., the solution of natural rubber in benzene). In the latter case the entropy of mixing is considerable because of the flexibility of the chain molecules of the polymer. When the long chain molecules of polymer are diluted with small solvent molecules, the number of configurations existing in the system of flexible chain molecules increases, since the concentration of chains decreases and consequently each of these is allotted a larger volume (the small molecules of solvent surrounding the chain molecule cause no serious hindrance to its thermal motion). This additional entropy of mixing is great enough for the appearance of solubility even with the absorption of heat.

However, in the case of mixing two polymers which have chain molecules of equal length and flexibility, no additional configurations are brought about by the mixing, since the mutual interferences are the same in the pure polymers as in the mixed polymers. Consequently, the entropy of mixing will be determined only by the change in the number of rearrangements of the molecules of the two types in the transition from the pure components to the solution. Thus the entropy of mixing should be the same for all systems containing equal numbers of molecules of two types, provided only that both types of molecules are alike in their geometric characteristics (in our case, provided both polymers possess chain molecules of equal geometric dimensions and equal flexibility; the difference between these may consist only in the characteristics of their chain structure or the differences in composition).

From the discussion above it follows immediately that with a rise in the molecular weight of both the mixed components, the role of the entropy term in the equation for free energy of mixing should decrease. Actually, although

the heat of mixing of two molecules, taken in amounts of two moles, for instance, will increase steadily with the molecular weight, nevertheless the entropy of mixing will remain the same since the number of mixed molecules here is constant.

Consequently, when both polymers have a sufficiently large molecular weight, their mutual solubility or insolubility should basically be determined solely by the sign of the heat of mixing. From this it follows immediately that even when the endothermic effect of mixing is small, the mutual solubility of the polymers should be limited. These considerations, which agree fully with the contemporary statistical theory of polymer solutions⁶, make it possible to understand why the majority of polymers are mutually insoluble and separate into two phases both in mixed stocks and in mixed solutions.

CONCLUSIONS

1. Mixtures of rubbers and raw rubber stocks prepared from a combination of two rubbers possess anomalous properties in a number of cases, revealed in the appearance of a maximum in the curve of the viscosity of such a system in relation to the proportions of the rubbers.

2. A mixture of solutions of different rubbers equal in concentration in a common solvent separates into two phases in the majority of cases, thus demonstrating the limited mutual solubility of the rubbers. This separation does not take place if the solutions are dilute enough so that the molecules of the two solvents enter into practically no reaction with one another. For a given pair of polymers, the minimum concentration at which the separation still takes place depends on the nature of the solvent.

3. In agreement with present-day theoretical opinion on the solubility of polymers, the results obtained demonstrate the decisive part played by interactions between the chain molecules, i.e., by the heat of mixing; and the insignificant part played by changes of entropy in the process of mutual solution of two polymers possessing chain molecules of equal size and flexibility.

4. The study of mixed polymer solutions is a valuable source of information on the mutual solubility of polymers. The experimentation carried out on rubber solutions confirms the mutual insolubility of a number of pairs of rubbers which was observed earlier in the study of the mechanical properties of vulcanizates prepared from mixed rubbers¹.

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- ² Kargin, V. A., and Sogolova, T. I., *Zhur. Fiz. Khim.* **23**, 540 (1949); Bartenev, G. M., *ibid.* **24**, 1210 (1950).
- ³ The viscosity values which we obtained cannot, of course, be considered absolute values. The effect of the borderline conditions in monoaxial compression distorts the measured values to some extent. However, an absolute viscosity determination was not required for our purposes; it was only necessary to compare the changes in viscosity in the transition from one ratio of rubbers to another, for which purpose it was possible to neglect the above inaccuracies.
- ⁴ Kargin, V. A., and Sogolova, T. I., *Zhur. Fiz. Khim.* **23**, 532 (1949).
- ⁵ The system SKS-30 + SKB has some very interesting features which will be considered in detail in subsequent work.
- ⁶ Gee, G., *Quart. Rev. Chem. Soc. (London)* **1**, 265 (1947).
- ⁷ Figure 3 which illustrated this behavior was too indistinct to reproduce with this translation.

THE MUTUAL SOLUBILITY OF POLYMERS.

III. HEATS OF MIXING OF POLYMERS *

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The study of the properties of polymer mixtures has become more and more necessary for the utilization of their various qualities to the fullest extent. This is still more important from the standpoint of industrial demands for materials possessing specific properties, which have given rise to numerous attempts to apply mixtures of polymers so as to combine the properties of the components of the mixtures. Such experimentation is essential also for the further development of theoretical conceptions regarding the relations between the structure of polymeric compounds and their mechanical, thermodynamic and other physico-chemical properties. The few research works presently available relating to the properties of polymer mixtures, in the great majority of cases, have significance only for a particular problem. However, present-day conceptions regarding the physico-chemical properties of polymers and the thermodynamic properties of solutions of these make it possible to assume¹ the existence of a simple relation between the heats of mixing and the mutual solubility of amorphous polymers.

It has been shown during the past 15–20 years² that many linear polymers (rubbers, polystyrene, polyvinyl chloride, polyvinyl alcohol, cellulose and its derivatives) have liquidlike structures. These polymers have been called amorphous polymers. Consequently, the mixture of two amorphous polymers should be considered as the mixture of two liquids. Even though amorphous polymers possess properties greatly different from those of ordinary low molecular weight liquids (i.e., elasticity), such a mixture can nevertheless be considered as a two-component liquid system.

The isothermal process of spontaneous mixing of two mutually soluble liquids under conditions of constant pressure is accompanied by a decrease in the thermodynamic potential ΔF . The change in the thermodynamic potential in the course of the mixing results from the change in the heat content ΔH and in the entropy ΔS , since these values are related by the thermodynamic equation

$$\Delta F = \Delta H - T\Delta S$$

where T is the absolute temperature. Many researchers have shown that the process of dissolving a polymer in a low molecular weight liquid is accompanied by a change in entropy, which exceeds by many times the corresponding values for ideal solutions³.

As was theoretically demonstrated by Flory and Huggins⁴, this difference is due to the flexibility of the long chain molecules, which results in a sharp increase in the number of configurations of such molecules during the dilution of the polymer with a liquid having small molecules.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from *Zhurnal Fizicheskoi Khimii* 30, 9, 1941–1947 (1956).

However, in the case of dissolving one polymer in another, the miscible molecules of the two types differ less from each other in their dimensions, and therefore the change in entropy during the mixing process should be closer to the ideal, and, in the case where chain molecules of identical length and flexibility are mixed together, will be equal to it. This change in entropy as related to one gram of the mixture will be insignificantly small as a result of the large molecular weight of the polymers being mixed.

At the same time, according to contemporary views the change in heat content as related to one gram of the rubber is of the same order of magnitude for polymers as for the mixing of low molecular weight liquids of the same composition and structure. In one gram of the material there will be approximately the same quantity of energetically reacting groups in both cases.

On the basis of these considerations, one can assume⁵ that the possibility of a mutual solution of the polymers will be determined in practice by the sign of the heat effect of mixing.

This hypothesis conforms to the present-day statistical theories of polymer solutions, and makes it possible to understand many of the anomalies revealed earlier during the study of the mechanical properties of polymer mixtures. It was of great interest, therefore, either to confirm or to refute this hypothesis by way of direct experimental data on the heats of mixing one polymer with another, and this was achieved in the present work. It may be mentioned that it is impossible to determine the heats of mixing of polymers directly because of their high viscosity. However, it is possible to calculate the quantity of heat of the mutual mixing of polymers from the corresponding complex of experimental data by the use of G. I. Hess' law that the heat effect is independent of the course of the mixing process.

And so, for instance, in order to find the heat Q_x evolved by the mixing of 1 gram of polymer A with 1 gram of polymer B, according to Hess' law it is sufficient to determine the heats of solution or of mixing in the following processes⁶:

I. Dissolving 1 gram of polymer A in 100 grams of solvent, with the formation of 101 grams of solution A, and the evolution of the heat Q_1 .

II. Dissolving 1 gram of polymer B in 100 grams of solvent, with the formation of 101 grams of solution B and the evolution of the heat Q_2 .

III. Mixing 101 grams of solution A and 101 grams of solution B, with the formation of 202 grams of solution (A + B) and the evolution of the heat Q_3 .

IV. Dissolving 2 grams of the mixture (A + B) in 200 grams of solvent, with the formation of 202 grams of solution (A + B) and the evolution of the heat Q_4 .

It is seen that the desired heat Q_x (under conditions of constant pressure or volume in the processes mentioned) may be found from the equation

$$Q_x = Q_1 + Q_2 + Q_3 - Q_4$$

This method of measuring heats of mixing of polymers calls for a high degree of accuracy in the measurement, since the values to be measured are not very large, and the value to be determined is the difference between values which are close together. However this method makes possible the determination of the heats of solution of individual polymers, which is of particular interest. Just for this reason, we have chosen this method of determining heats of solution in polymers, in spite of the obvious experimental difficulties.

The selection of samples for investigation was subject to the following considerations: since the most thorough study of physico-mechanical properties of polymer mixtures made up to the time of our work had been carried out on a mixture of rubbers, another group of polymers was chosen for study. It was of interest to investigate the types of interactions found in various kinds of polymers which are important in industry; therefore, various cellulose esters and various examples of polyacrylates and polymethacrylates, polystyrene and polyvinyl acetates were studied.

EXPERIMENTAL PART

A series of stepwise determinations of the heats of solution of polymers and mixtures of these, as well as of the heats of mixing of polymer solutions, has been taken as a basis for the experimental part of this work.

The measurements were carried out in an adiabatic calorimeter of ordinary construction. The calorimetric vessel, with a 300 cm³ working capacity, was made from sheet copper, thoroughly polished and then nickel plated. This vessel was placed on a heat-insulated stand and inserted in a metal container whose outer jacket was washed with water. The water temperature in the jacket of the calorimeter was kept equal to the temperature of the calorimetric vessel by means of adding hot or cold water.

The sample for experimentation, contained in a special ampoule, was first kept for a certain period of time in the jacket of the calorimeter, after which it was immersed in the solvent contained in the calorimetric vessel. In addition to this main method of introducing the substance into the calorimeter, other methods were also employed in separate cases.

The rise in temperature⁷ was registered by a thermometer calibrated in divisions of 0.005° C. Observation of temperature variations with a magnifier increased the reading accuracy up to 0.001° C.

The water temperature in the jacket was maintained with the same degree of accuracy. The liquids in the calorimetric vessel and jacket were agitated thoroughly with a stirrer. The thermal value of the calorimetric system was determined by an electric method, namely by passing a constant electric current through the heater immersed in the calorimeter liquid. The voltage and current intensity were measured on the heater terminals by a voltmeter (accuracy rating 0.1) and a milliammeter (accuracy rating 0.1), respectively. The time of the current flow was measured with a stopwatch which was accurate within 0.2 second. The stopwatch was set in motion automatically at the moment the current of the heater was switched on.

For mixing two solutions of polymers a special glass ampoule equipped with a three-way stopcock was employed. The ampoule was filled with one of the solutions to be mixed and was immersed in the jacket. The mixing of the solution in the ampoule was accomplished by passing through it air bubbles pre-heated to the required temperature in a metal coil installed in the jacket.

The other polymer solution was poured into the calorimetric vessel, thus only half filling it. At the starting moment of the main test period, the ampoule was connected with the calorimetric vessel by turning the three-way stopcock, and in this way the solutions to be mixed were brought into mutual contact. The solvents used here were first dehydrated, filtered and distilled.

The polymer samples were purified preparatory to the determination of their heats of solution in the solvent. The basic method of purification which we used involved precipitation of the polymer out of the solution by the addition of a non-solvent. In this way the polymer sample was freed of all the possible

monomeric contaminants, low molecular weight fractions, stabilizers and other soluble low molecular weight substances contained in the polymer at the moment of polymerization. In the case of synthetic rubbers we worked with industrial polymers, because the purification of these led to a loss of solubility resulting from the strong oxidation which developed after the removal of anti-oxidants during the purification process.

Special attention was paid to the preparation of polymer mixtures, since the achievement of equilibrium was quite difficult on account of their high viscosity. In this connection, it became necessary to clarify the effect of any given method of preparation of a mixed polymer stock upon the heat of solution of the mixture.

We have investigated mixed polymers prepared in a variety of ways, namely by means of: (a) milling on a rubber mill, (b) milling and extrusion followed by a period of relaxation at an elevated temperature, (c) milling fol-

TABLE I
INTRINSIC VISCOSITIES OF POLYMER SOLUTIONS

Polymer	Abbreviated designation of polymer*	Solvent	Intrinsic viscosity
Sodium-butadiene (polybutadiene) rubber	SKB ¹	Benzene	1.70
Butadiene-styrene rubber	SKS-30	Benzene	1.50
Natural rubber	NR	Benzene	3.40
Nitrocellulose (11.9% N)	N.Cel.	Acetone	1.90
Cellulose acetate (56% acetyl groups)	Cel.Ac. (56%)	Acetone	2.00
Cellulose acetate (48% acetyl groups)	Cel.Ac. (48%)	Acetone	1.25
Benzylcellulose	B.Cel.	Chloroform	1.40
Polystyrene ¹	P.Styr. ¹	Benzene	2.90
Polystyrene ²	P.Styr. ²	Benzene	—
Polystyrene ³	P.Styr. ³	Benzene	Mol wt, 22,400
Polyvinyl acetate ¹	P.V.Ac. ¹	Acetone	1.77
Polyvinyl acetate ³	P.V.Ac. ³	Acetone	1.92
Polymethacrylate	P.M.Acr.	Acetone	3.30
Polycaprolactone	P.B.Acr.	Acetone	1.00
Polyethylmethacrylate	P.M.M.Acr.	Acetone	1.30
Polybutylmethacrylate	P.B.M.Acr.	Acetone	5.10

(The upper index number indicates the batch number of the polymer.)

* These abbreviated designations will henceforth be used throughout.

lowed by prolonged aging, (d) evaporation of the solvent from a mixture of concentrated polymer solutions, and finally (e) precipitation from the mixture of solutions.

Experiments have shown⁸ that the preliminary purification of the initial polymers, as well as the method of preparation of a polymer mixture, in some cases cause a great change in the heat of solution of a given polymer or mixture of polymers, while in other cases this has no effect at all.

In order to exclude this influence, both the polymers and mixtures of these were subjected to methods of purification and processing with identical conditions. Measurements of the relative viscosity of the dilute polymer solutions were carried out at 5–6 different concentrations not exceeding 1%, to show the individual characteristics of the polymers being studied.

The intrinsic viscosity [η], whose value was adopted as a basic characteristic of a polymer, was determined by the graphic extrapolation to zero concentration of the curve of viscosity versus concentration (Table I).

TABLE II
INTEGRAL HEAT OF MIXING OF THE POLYMERS

Name of polymer	Q_1 , cal/g	Heat of solution of polymer		Common solvent of both polymers	Heat of mixing of polymer solutions, Q_t , cal/2 g of polymer	Heat of mixing of mixed polymer stocks, Q_s , cal/2 g of stock	Heat of mixing of polymers, Q_a , cal/2 g of stock
		Name of polymer	Q_1 , cal/g				
SKB ¹	-1.55	SKS-30*	-0.73	Benzene	0	-2.75	+0.5
SKB ²	-1.73	P.Styr. ¹	+6.55	Benzene	0	+4.50	+0.3
SKB ³	-1.73	P.Styr. ²	+5.47	Benzene	0	+3.18	+0.6
SKB ⁴	-1.66	Ethylbenzene	-1.08	Benzene	0	-2.37	-0.4
NR	-2.38	SKB*	-1.55	Benzene	0	-4.26	+0.3
NR	-2.38	SKS-30*	-0.73	Benzene	0	-2.85	-0.3
B.Cel.*	+3.47	P.Styr. ^{3*}	+6.88	Cyclohexanone	0	-11.60	-1.3
B.Cel.	+8.95	P.Styr. ³	+3.96	Chloroform	0	+16.78	-3.9
N.Cel.	+18.78	Cel.Acr.	+10.65	Acetone	0	+23.56	+5.9
(56%)							
N.Cel.	+18.78	P.B.Acr. ¹	+0.68	Acetone	0.25	+18.36	+0.9
Cel.Acr. (56%)	+10.65	P.V.Acr. ¹	+0.68	Acetone	0	+14.24	-2.9
Cel.Acr. (56%)	+10.65	Cel.Acr.	+8.46	Acetone	-0.36	+26.70	-8.0
(48%)							
P.M.Acr.	0	P.B.M.Acr.	-2.44	Acetone	-0.66	-3.13	0
P.M.Acr.	0	P.M.M.Acr.	+7.12	Acetone	-0.40	+9.26	-2.5
P.B.Acr.	-0.2	P.B.M.Acr.	-2.44	Acetone	0	-2.07	-0.6
P.M.M.Acr.	+7.18	P.B.M.Acr.	-2.44	Acetone	-0.25	+4.78	-0.3
P.V.Acr.*	+0.18	P.M.M.Acr.*	+1.52	Acetone	-0.24	+2.57	-1.0
P.V.Acr. ¹	+0.68	P.B.Acr.	-0.2	Acetone	-0.53	+0.39	-0.4

* Tested without previous purification.

The heats of solution of the polymers are shown in Table II. The table has been compiled from experimental data obtained by us from determinations of heats of solution of polymers and mixtures of these in low molecular weight solvents as well as of heats of mixing of the solutions.

The formerly unknown heat of mixing of the polymers was determined as indicated above, with the equation $Q_x = Q_1 + Q_2 + Q_3 - Q_4$.

In addition to the measurement of the heats of solution of polymers, it was also necessary to characterize the physical condition of these mixtures. For this purpose the behavior of mixtures of solutions of the corresponding polymers was studied⁹. Only one basic characteristic of the solutions was studied, namely the presence or absence of a separation into two phases. It is evident from Table III that the mutual mixing of the great majority of polymer pairs results in a separation of the solutions into two phases.

TABLE III
BEHAVIOR OF MIXED POLYMERS IN A COMMON SOLVENT

Polymers	Solvent	Behavior of mixture of solutions
SKB + SKS-30	Benzene	Separates into layers
SKB + SKS-30	Gasoline	Separates into layers
SKB + P.Styr. ¹	Benzene	Separates into layers
SKB + P.Styr. ²	Benzene	Separates into layers
SKB + Ethylbenzene	Benzene	Dissolves
Natural rubber + SKS-30	Benzene	Separates into layers
Natural rubber + SKB	Benzene	Dissolves
B.Cel. + P.Styr. ¹	Cyclohexanone	Separates into layers
B.Cel. + P.Styr. ¹	Chloroform	Separates into layers
N.Cel. + Cel.Ac. (56%)	Acetone	Dissolves
N.Cel. + P.V.Ac. ¹	Acetone	Dissolves
Cel.Ac. (56%) + Cel.Ac. (48%)	Acetone	Separates into layers
Cel.Ac. (56%) + P.V.Ac. ¹	Acetone	Separates into layers
P.M.Acr. + P.B.M.Acr.	Acetone	Separates into layers
P.M.Acr. + P.M.M.Acr.	Acetone	Separates into layers
P.M.Acr. + P.B.M.Acr.	Acetone	Separates into layers
P.M.M.Acr. + P.V.Ac. ²	Acetone	Separates into layers
P.M.M.Acr. + Cel.Ac. (56%)	Acetone	Separates into layers
P.V.Ac. ¹ + P.B.Acr.	Acetone	Separates into layers
Cel.Ac. (48%) + P.V.Ac. ²	Acetone	Separates into layers
P.B.Acr. + P.B.M.Acr.	Acetone	Separates into layers

DISCUSSION OF RESULTS

The object of the present work was to discover to what extent the assumption that the sign of the heat of mutual mixing of two polymers is the determining factor in the process of mutual solution of polymers, conforms to reality. The data given show that the great majority of polymers are endothermally miscible, and that the mixtures of solutions of these with equal concentrations hence separate into two phases. Thus the mixing of polymers in many cases appears to be out of equilibrium and occurs only as a result of their huge viscosity which interferes with a macroscopic separation. This separation does, of course, occur in fairly small volumes as a result of the mobility of the separate sections of the flexible molecules, which causes an extremely fine nonhomogeneity in the mixture. Therefore, the exceptional pairs of polymers listed below, which are miscible exothermally and do not form separate layers in solution, are of particular interest: natural rubber with sodium-butadiene (polybutadiene) rubber (SKB); nitrocellulose (nitrogen content 11.9%) with cellulose acetate

(acetyl group content 56%) and with polyvinyl acetate. It is evident that these mixtures can be obtained in a homogeneous and stable form.

It should also be pointed out that even polymers which are closely similar in their structure and composition, such as, for instance, the two cellulose acetates with a different content of acetyl groups (56% and 48%) are mutually insoluble. At first glance, the mixtures of SKS-30 and of polystyrene with sodium-butadiene rubber (SKB) appear to present a very strange and interesting anomaly; they are formed with an evolution of heat even though mixtures of their solutions separate into layers. A detailed discussion of this anomaly will be given in a subsequent communication.

Thus we have demonstrated that the sign of the heat actually does govern the mutual solubility of polymers, with the exception of the two anomalous pairs. We may note that the above-mentioned anomalous pairs also conform to this general law, as will be demonstrated later on.

Considering the widespread use of polymer combinations in industrial applications, it is necessary to give more attention to a systematization of the collected data on the behavior of polymer mixtures. Furthermore, it should be taken into consideration that the macroscopic combination of polymers in most cases does not amount to a microcombination, and hence such mixtures are micrononhomogeneous.

The present-day theory of polymer solutions is sufficient to make possible further theoretical and practical studies based on the laws we have discovered.

CONCLUSIONS

- Measurements of the heats of mixing as between different polymers, which we have carried out, have confirmed the correctness of the assumption that the heat effect plays a decisive part in the process of mutual mixing of polymers.

- The anomalous behavior of mixtures of SKS-30 with SKB and polystyrene with SKB has been revealed.

- Experimental data on the heats of mixing of polymers, which has substantial value for theoretical and practical research in the field of polymer mixtures and for the evaluation of possible practical applications of these, has been collected.

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- If the heats Q_1 and Q_2 are of no interest per se, then it suffices to determine the heats of solution in two processes: 1. The simultaneous solution of 1 gram of A and 1 gram of B in 200 grams of solvent, with the formation of 202 grams of solution (A+B) and the evolution of the heat Q_1^* . 2. Dissolving 2 grams of the mixture (A+B) in 200 grams of solvent with the formation of 202 grams of solution (A+B) and the evolution of the heat Q_2^* . Then $Q_s = Q_1^* - Q_2^*$.
- The rise in temperature here signifies both the increase and the decrease in temperature during the experimentation.
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- Two polymers were dissolved in a common solvent and then the solutions, of equal concentrations by weight, were mixed together in equal quantities and given lengthy observation. The concentrations of the solutions were high enough that the interaction between the molecules of the polymers was appreciable. On the other hand, these concentrations were such that the viscosity of the solutions did not offer any strong resistance to a separation into phases.

THE MUTUAL SOLUBILITY OF POLYMERS. IV. THE EFFECT OF THE PACKING DENSITY OF POLYMER MOLECULES ON THEIR MUTUAL SOLUBILITY *

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It was shown in a previous report¹ that when a sodium-butadiene (polybutadiene) rubber (SKB) is mixed with a butadiene-styrene copolymer (SKS-30) or with polystyrene, it does not conform to the general rule of polymer mixing, which is that where the heat of mixing of pure polymers is positive, solutions of these with equal concentrations when mixed together form a one-phase system, whereas when the sign of this heat value is negative the solutions separate into two phases. The peculiarity of the two systems mentioned is that a mixture of solutions of these separates into two phases although the heat of mixing of the polymers is positive.

The purpose of the present work is to consider the reasons for this anomaly. It should be pointed out at the outset that both systems possess styrene groups. In connection with this it may be recalled that Tager and Kargin² showed, through an experimental study of the heats of solution of polystyrene in ethylbenzene, that the heat evolved when a polymer is dissolved in the hydrogenation product of its monomer is due to the looseness of packing which exists in the chain molecules in cases where the polymer molecules are not sufficiently flexible.

Klimenkov, Kargin and Kitaigorodskii³ found by calculation that the transition from the monomeric to the polymeric state involves a smaller change in volume in polymers with rigid chains. Thus the packing density of polymers is determined to a considerable extent by the flexibility of the chains, rather than by the intermolecular interactions of the chain molecules.

Since the packing density governs the specific volume of the polymer, and changes in the volume are closely related in turn to the heat effects, then it is natural to assume that the anomaly which we observed in the behavior of polymer mixtures is due to the effect of the packing density of the molecules on the magnitude of the heats of mixing of the polymers.

The anomaly which we have noted is characterized by the data given in Table I. This table shows that while the heats of mixing of SKB with SKS-30 and of SKB with polystyrene are definitely positive, nevertheless mixtures of solutions of these separate into two phases. This contradiction is all the more remarkable since the behavior of raw mixed polymers and cured stocks prepared from a combination of SKB and SKS-30 rubbers, according to earlier work⁴ indicates that these rubbers have a limited mutual solubility.

Thus the data from the mechanical testing of mixed polymers and cured stocks and the behavior of solutions of these polymers agree with one another, but they contradict the results of heat of mixing measurements. The separation into two layers by mixtures of solutions of these rubbers with equal con-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from *Zhurnal Fizicheskoi Khimii* 30, 10, 2144-2148 (1956).

centrations indicate that when such molecules are mixed together heat must be absorbed, i.e., that the heat effect of mixing the solutions is negative⁵. The micro-nonhomogeneity of the cured stocks prepared from mixtures of SKB and SKS-30 likewise shows that at the vulcanization temperature (143° C) a micro-stratification of the rubber stock takes place which then becomes fixed by the vulcanization bonds. The question logically arises: how is the heat evolved when SKB is mixed with SKS-30 or with polystyrene? It seems to us that the only possible source of the heat evolved in the mixing of SKB with SKS-30 and SKB with polystyrene might be the decrease in the volume of the system when its component parts are mixed together. Actually, the experimental data on the heats of mixing of SKB with polystyrene and of SKB with the hydrogenated monomer of polystyrene (ethylbenzene) shows that even with chemical groups of the same structure and composition, the signs of the heats of mixing here are different. Although SKB mixed with polystyrene evolves heat, the system SKB-ethylbenzene absorbs heat when mixed together. At the same time, however, it is known² that polystyrene dissolves in ethylbenzene with an evolution of heat because of the decrease in volume of the system polystyrene + ethylbenzene when the solution forms.

TABLE I
INTEGRAL HEATS OF MIXING OF POLYMERS AND THE BEHAVIOR OF
MIXED SOLUTIONS OF THESE IN BENZENE

Mixture	Heat of mixing of the polymers, calories per 2 grams of the mixed stock	Behavior of mixture of solutions of the polymers
SKB + SKS-30	+0.5	Separates into layers
SKB + Polystyrene ¹	+0.3	Separates into layers
SKB + Polystyrene ²	+0.6	Separates into layers
SKB + Ethylbenzene	-0.4	Dissolves

(The superscript indicates the batch number of the polymer.)

It is quite clear that if a loosely packed polystyrene evolves heat when mixed with ethylbenzene, then it should also evolve heat upon compression and when mixed with a polymer possessing flexible chain molecules, with SKB in particular. Thus the heat effect of mixing polystyrene with SKB may be resolved into two parts: heat liberated by the decrease in the volume of the system when the solution is formed, and heat absorbed at the same time through the increased energy of the molecular interaction resulting from a change in the composition of the system during the mixing process.

Naturally, in a case where the volume of the systems is kept constant during mixing, the heat effect is determined only by the second item mentioned, and in relation to 1 gram of stock this should be the same for a mixed stock composed of two polymers as for a mixture of two hydrogenated monomers of these polymers. Consequently, the change in the sign of the heat of mixing when ethylbenzene is used in place of polystyrene in combination with SKB indicates the essential role played by volume compression (contraction) in the mixing of these polymers.

In connection with the above, it was of interest to verify whether or not a difference in molecular weight has an important effect on the heats of mixing in a case where both polymers have densely packed molecules. In other words, it was necessary to prove that the heats of mixing of two polymers and of two

hydrogenated monomers differ only slightly from one another if the polymer molecules are flexible and hence are packed together just as densely as the molecules of their low molecular weight homologues.

For this purpose we determined the heat of mixing of ethyl acetate and butyl propionate, which are the hydrogenated monomers of polyvinyl acetate and polybutyl acrylate, respectively. These polymers were chosen because they dissolve in their monomers without any heat effect, i.e., they are densely packed. The heat of mixing of these two hydrogenated monomers is the same as that of the corresponding pair of polymers (polyvinyl acetate and polybutyl acrylate), and amounts to -0.4 calorie for 2 grams of the mixed stock. This clearly demonstrates that when the effect of a loose packing of the polymer molecules is absent, the heat effect for the same weight of sample actually depends but little on the degree of polymerization.

TABLE II
DENSITIES OF BUTADIENE-STYRENE COPOLYMERS AND
MIXED POLYMER STOCKS
(From the data of Marei and Al'tshuler⁶)

Copolymers and mixed polymer stocks	Density, d_4^{20}	Styrene content	
		Introduced into the stock	Determined from the density
Polystyrene	1.054	—	100
Polystyrene + polybutadiene	1.036	90.0*	89.7
Polystyrene + polybutadiene	1.013	75.0*	75.0
Buna SS	0.978	—	51.8
Buna SS + polybutadiene	0.961	38.9**	40.5
Buna S	0.944	—	28.5
Buna SS + polybutadiene	0.942	25.9**	26.5
Polystyrene + polybutadiene	0.939	25.0*	24.5
GR-S	0.937	—	23.0
Buna SS + polybutadiene	0.925	13.0**	14.0
Buna SW-10	0.919	—	9.5
Polystyrene + polybutadiene	0.918	10.0*	9.0
Polybutadiene	0.907	—	0

* A mixed stock of polystyrene and polybutadiene prepared from mixed benzene solutions of the polymers.

** A mixed stock of Buna SS + polybutadiene prepared on a rubber mill.

Analogously to polystyrene, it would be logical to suppose that the butadiene-styrene rubber SKS-30 would also have loose packing, because of the presence of a considerable number of styrene groups in the molecule of this rubber.

A conclusive proof of our assumption of loose packing in the molecules of SKS-30 is offered by determinations of the density of butadiene-styrene copolymers and of mixtures of polystyrene with polybutadiene and with the copolymers, which were carried out by A. I. Marei and M. Z. Al'tshuler⁶. According to their data, a linear relation was observed between the specific volumes of the butadiene-styrene copolymers and their styrene content, in all the systems which they studied. It is easy to understand that, since polystyrene is loosely packed, then the packing in all copolymers of butadiene with styrene, and in particular in SKS-30, should also be loose; because in the opposite case there would be a deviation from linearity. Furthermore, a careful analysis of all the data given on densities (Table II) indicates that only very slight sys-

tematic deviations from the linear relation can be observed, which gives additional confirmation of our assumption.

The table shows that in the cases where the stock was prepared from solutions, the styrene content as determined from the density by the linear rule was found to be lower than (or in one case, equal to) the actual figures. When the stocks were prepared on a mill, however, the reverse was true in all cases—the calculated figures were higher than the true ones. From our point of view, this is as it should be. Our experiments have shown that when polymer mixtures are prepared from solutions which have separated into two phases, the density of such a micro-nhomogeneous stock should actually decrease by reason of the loosening up of the material which takes place in the process of separation of the solution into two phases. Hence the styrene content as estimated by the use of the linear rule should be low. However, when the material is mixed on a rubber mill it becomes more dense through contraction, and this causes high results in the determination of styrene in the stock.

Although we do not consider the evidence given to be conclusive, we do think it probable that a contraction of the volume might be possible in the mixing of SKB with SKS-30. In our opinion it is exactly this which explains the positive sign of the heat of mixing of SKB with SKS-30. However, when polymer solutions are mixed the total volume of the system does not change, and therefore it is quite natural that mixed solutions of SKB with SKS-30 or SKB with polystyrene should separate into two phases, since the heat of contraction had already been liberated earlier when the solutions were prepared and thus should play no part in the mixing of the solutions.

In this way the discrepancy which we had observed earlier between the rule governing the heat effect of mixing in the systems SKB + SKS-30 and SKB + polystyrene, and the behavior of these systems in mixtures of their solutions is now entirely eliminated.

It remains to consider the reason for the appearance of microstratification in cured stocks prepared from a combination of SKB and SKS-30. We may note that the loose packing in SKS-30, which is related to the presence of styrene groups in the molecules of this rubber, should decrease at temperatures above the softening region of polystyrene. Hence at such temperatures the heat of mixing of SKB with SKS-30 should become negative, since its positive component, which is due to a contraction of the volume, ceases to be appreciable here. Consequently in systems of a similar type the critical temperature of mixing should be lower; i.e., it should be a little above the temperature at which a looseness of packing ceases to prevail. In our case this should correspond to the vitrification temperature of the polystyrene ($+80^\circ\text{C}$), since the looseness of packing in SKS-30 can only be due to the insufficient flexibility of the styrene portions of the chain molecules of this rubber.

Hence at the vulcanization temperature ($+143^\circ\text{C}$) SKB and SKS-30 should have a limited mutual solubility, since this temperature is above the lower limit of the critical temperature. It is natural that the microstratification which occurs here becomes fixed in the vulcanizate structure, as was also observed in the study of mechanical properties of such cured stocks⁷.

From what has been said above, it may be assumed that with a sufficiently rapid vulcanization (where there is not enough time for the stratification to take place) or with a low-temperature vulcanization (below the critical temperature) it would be possible to obtain completely homogeneous cured stocks based on a combination of SKB with SKS-30.

The conclusion which we have drawn in our work as to the great magnitude of the volume contraction occurring when loosely packed polymers are mixed together, which makes it possible to understand a number of discrepancies which we and other research workers have observed, should be taken into consideration in the further development of the theory of solutions of one polymer in another, i.e., in the study of the processes that take place when polymers are mixed.

It must be emphasized also that the looser packing of polymers with rigid molecules can be either an equilibrium or a nonequilibrium state. In the latter case some unusual processes can take place, e.g., the complete solution of a loosely packed polymer (forming a homogeneous solution) followed by the precipitation of the same polymer from the solution in the form of a more densely packed solid phase. Consequently, thermodynamic concepts are of limited application to such polymers.

CONCLUSIONS

1. It is pointed out that the decrease in volume plays an important part in the mixing of polybutadiene rubber (SKB) with butadiene-styrene rubber (SKS-30) and of polybutadiene rubber with polystyrene. In this connection it is emphasized that the assumption of volumes being additive in the mixing of polymers is limited in application.

2. It was shown that the heat effects of the mixing of polymers does not depend on the degree of polymerization, provided that no contraction takes place in mixing, and that the sign of the heat effects can even be changed if the packing of the molecule becomes more loose as the degree of polymerization increases.

3. From a theoretical analysis of experimental data found in the literature the opinion was advanced that the critical mixing temperatures for the systems polybutadiene rubber-butadiene-styrene rubber and of polybutadiene rubber-polystyrene are low, being somewhat above the vitrification temperature of polystyrene. The existence of lower critical mixing temperatures here is caused by a decreased packing density in the molecules of polystyrene and of butadiene-styrene rubber at temperatures below the vitrification temperature of polystyrene.

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THE OXIDATIVE SOFTENING OF SYNTHETIC RUBBER LATEX *

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The present work was begun in 1944 in the main laboratories of the Buna-werke GmbH in Schkopau and was interrupted in April 1945. At the beginning of our investigations we were already aware of certain factors indicating that elaboration of the problems involved was desirable, especially since an eventual improvement of rubber fabrication methods was indicated. For personnel reasons the investigations were not resumed until 1952, when the large-scale production of Buna S4 and other softened butadiene copolymers was taken up by the VEB Chemische Werke Buna.

INTRODUCTION

Mechanical breakdown.—Both natural rubber and synthetic rubber must be plasticized before processing. Otherwise, due to their nerve, they can be worked only with extreme difficulty on a mixing mill. In the case of natural rubber this softening (cf. Figure 1) is achieved in a short time through mastication, whereas Buna S3 can be broken down only under highly favorable conditions (well-cooled and closely-set "tight-nip" rolls, small batches, etc.). Mastication of synthetic rubbers has consequently remained technically unimportant. Only the incorporation of mastication aids permits a technically satisfactory softening, especially with Buna N types. One might mention, as classes of softeners, the thiophenols and phenylhydrazines¹. When this chemical-mechanical plasticizing procedure is applied to the butadiene-styrene copolymers of the Buna S1 and Buna S3 types, softening does occur, but generally there is a falling off in the physical properties of both the plasticized raw material and the compounds made therefrom. Besides, almost all agents promoting mastication have some objectionable physiological features².

In 1937 a new method was discovered for plasticizing Buna S1, known as thermal breakdown. Mastication of natural rubber and thermal breakdown of Buna have the same purpose: reduction of elasticity and increase of plasticity.

Thermal breakdown.—If Buna S is heated in the presence of air or oxygen, a softening ensues, manifesting itself in increased plasticity and a diminishing viscosity of its solutions. As the breakdown time increases, the plasticity tends toward a maximum, beyond which it drops off and the material begins to harden (Figure 2). In this thermal softening, two opposing, overlapping processes are involved. The degree and rate of softening depend on a whole series of factors that have often been the subject of investigations, the particulars of which will not be gone into here³. Nevertheless, it should be pointed out that technical mastery of thermo-oxidative softening and its reproducibility is possible only with a sufficiently stabilized synthetic rubber. In the

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by George Leuca from *Kautschuk und Gummi*, Vol. 10, No. 7, pages WT 161-167 (1957). This is a modified version of a translation for the Goodyear Tire and Rubber Co., Akron, Ohio.

European rubber-processing industry thermo-oxidative breakdown has become a precisely developed unit process consuming not a little power and requiring large installations and equipment.

Plasticity control through control of polymerization.—With regard to polymerization, so-called modifier control was later introduced to produce soft

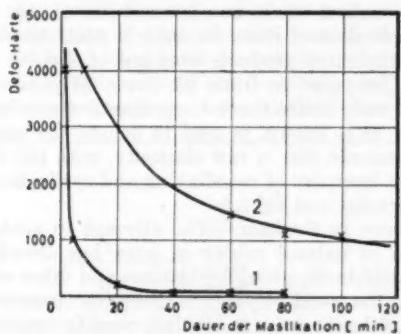


FIG. 1.—Mastication of natural rubber and Buna S3 (250 g of material on a cold, tight-nip laboratory mill). Curve 1—natural rubber; Curve 2—Buna S3. Abcissa axis: mastication time; ordinate axis: Defo hardness.

rubber during polymerization, i.e., shorter and less strongly crosslinked polymer chains⁴. The American synthetic rubber industry, during its expansion in 1939–40, went ahead on this road pioneered by German industry, thus circumventing thermo-oxidative breakdown. This led to GR-S. In Germany the

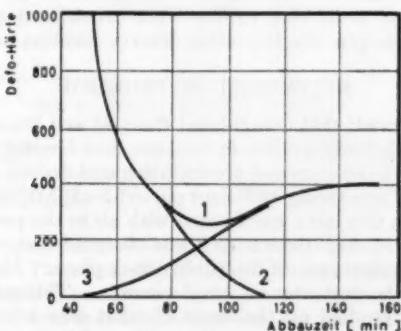


FIG. 2.—Thermal softening and hardening. Curve 1—degradation curve; Curve 2—course of softening reaction; Curve 3—course of hardening reaction. Abcissa axis: degradation time; ordinate axis: Defo hardness.

introduction of modification (regulation) resulted in Buna S3 (1944) and then Buna S4 (made at Schkopau since 1952). Plasticity control through modifier control of polymerization has also been realized for butadiene-acrylonitrile copolymers. Buna S4, Buna NW, and others can be processed directly on rubber mills and mixers without prior thermo-oxidative breakdown.

Regulated or modifier controlled polymerization brought with it, however, certain disadvantages as compared to unregulated polymerization. First of all, polymerization was slowed down and, secondly, there was a worsening in certain physical-chemical properties of the polymer compounds. Even though losses in polymerization rates could be compensated for by "strengthening" the recipe, nevertheless the elasticity, for example that of Buna S4 vulcanizates heavily loaded with carbon black, was lowered irreversibly by several points. This limited the application of Buna S4, since it could be used only where the elasticity values of the cured products were not of decisive importance in the finished product. Compared to Buna S3, Buna S4 possesses a considerably better processibility and, unlike the former, does not exhibit this so-called recovery. This term, as is known, is used to denote the renewed drop in raw plasticity and the renewed rise in raw elasticity, with the storage time. Recovery represents an interplay of crosslinking and cyclization reactions, and is a function of temperature and light.

Chemical breakdown in the latex.—The attempt to achieve a softening of Buna S3 as well as of natural rubber in latex has already been made, for example, with thionaphthols, phenylhydrazines and other substances. Natural rubber latex was the usual polymer in these experiments⁵. Peptizers were added to the latex, either in order to obtain a more favorable mastication after precipitation of the rubber, or to soften the rubber in the latex stage without subsequent mastication. The use of this softening procedure in synthetic rubber latex, however, caused a simultaneous drop in the physical properties of the resulting soft rubber. An after treatment⁶, discussed in U. S. Patent 2,206,448, in which the peptizing agents hydrogen peroxide and phenylhydrazine are specified, demonstrated that the technological properties of the resulting rubber were worse than those of thermally-degraded Buna. The stability in storage of the former was also very poor, and strong recovery phenomena were in evidence. Among the multitude of chemical compounds named in patents as protecting rubber from breakdown in the presence or absence of air and oxygen, the thio acids deserve mention here.

STATEMENT OF PROBLEM

It has been observed⁷ that unregulated Buna S1 and Buna S3, as they occur in latex, are still relatively soluble in benzene, but become increasingly more difficult to dissolve in the course of precipitation and drying, in spite of the fact that, in all stages of processing, sufficient phenyl-2-naphthylamine is on hand as antioxidant. When this latex was treated with air in the presence of oxidation catalysts and phenyl-2-naphthylamine it was observed that in time an oxidative breakdown, albeit a slow one, of the rubber took place. Metal sols were used as oxidation catalysts, and later on, alkyl phenols. This softening reaction in the latex was now studied on the basis of what was known about thermo-oxidative breakdown of Buna S1 or Buna S3, and its variations were determined. Especially the resulting soft rubbers were subjected to a searching investigation of their technical applications in order to keep track of the degree of improvement or deterioration in properties. It was discovered thereby that when the two above-named oxidation catalysts were used, the physical-chemical properties of Buna S3 broken down in the latex were practically identical with those of thermally plasticized Buna S3. The unwanted recovery was still present. That is why the method developed for softening in the latex seemed unimportant at the time⁷. It presented no apparent advantages

over breakdown of the solid material. The German rubber processing industry was set up for thermal degradation of Buna S3, and there was no thought of curtailing that system of operation.

However, the situation changed when, in 1952, mass production of highly-regulated Buna S4 was begun along with continued production of Buna S3. Since both rubber types had to be produced within a short space of time, one after the other, for the market demand, and in the same polymerizer batteries, the charging and discharging of these reactors caused an important drop in production. Thus the latex breakdown process we had worked out in former years came into its own again around this time, especially since it had been established that the elasticity values of the black-filled vulcanizates of Buna

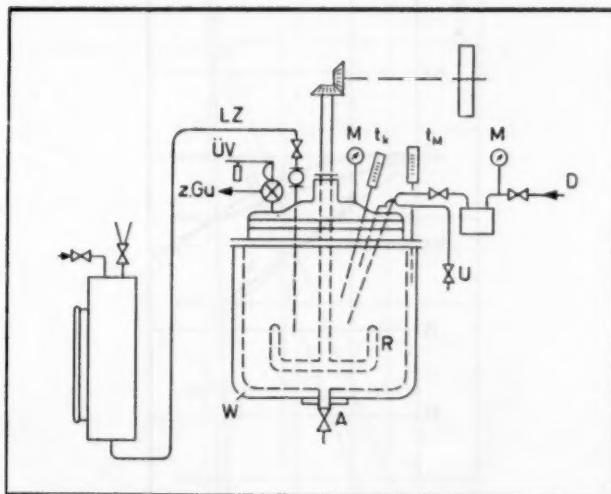


FIG. 3.—Pressure vessel with stirring device.

R stirrer
A outflow cock
M manometer
W hot water (or steam) jacket
 t_k inside thermometer
 t_M outside thermometer

U overflow
ÜV excess pressure valve with
gas meter connection.
LZ latex inflow
z.Gu to the gas meter
D compressed air

S3 which had been broken down in the latex were better than those of mass-produced Buna S4. Then too, the question of recovery, already mentioned, needed to be investigated anew.

With this turn of events it seemed possible for us to achieve a continuous breakdown in the latex, thus freeing our polymerizers from the production of Buna S4 types. We considered diverting, from the continuous production of Buna S3 latex, a partial stream in a countercurrent reaction tube for the purpose of breaking it down in the latex, to the plasticity of Buna S4, that is to a raw Defo value of approximately 600–800. In the course of our work, however, this technical production problem was solved by a so-called "roundabout" polymerization control process, so that in the end only the cardinal question of a possible improvement in quality by means of latex softened Buna S3 as compared to Buna S4 was debated.

EXPERIMENTS ON A TECHNICAL SCALE

Apparatus.—An enameled 40-liter, pressure vessel with stirring attachments was used for the breakdown experiments (Figure 3). The vessel had a water jacket, connected to hot water and low pressure stream. This vessel, which was thoroughly cleaned each time, was charged with 20 kg of stabilized Buna S3 latex, with simultaneous addition of the oxidation catalysts needed. After the pot was closed, heat was applied, stirring was started, and there was subsequent pressurization with compressed air, first to 1 atm gage pressure, and then, after attainment of the desired reaction temperature, to 3 atm gage

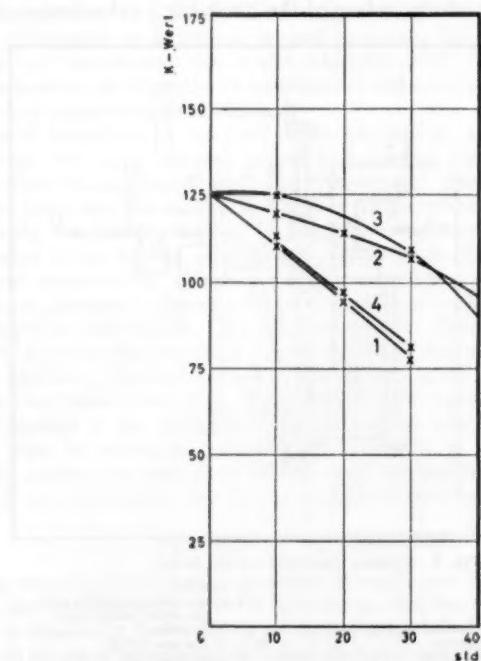


FIG. 4.—*K*-value as a function of the heating time at 80° C. Notation of curves: 1, latex with 0.0023% Co—3 atm O₂; 2, latex without Co—3 atm O₂; 3, latex with 0.0023% Co—3 atm N₂; 4, latex with 0.012% Co—3 atm O₂.

pressure. At intervals, a latex sample was drawn off through an outlet valve at the bottom. The rubber was precipitated in the usual way and tested in regard to its technical application. For the introduction of air the vessel had a pipe whose bottom part was drilled in a number of places. The release of air was automatic via an excess pressure valve, permitting the escaping air to be measured by a gas meter.

Treatment of rubber samples.—The latex samples taken at specified intervals were stirred with a magnesium chloride solution of about 20 per cent concentration to form a slurry that was introduced into a previously prepared aqueous precipitating solution with vigorous stirring. The solution was brought to a pH of 5.5 to 6.0 with acetic acid, and contained about one per cent ferrous

sulfate. The flocculated Buna crumbs were washed five times with generous amounts of water and then centrifuged. The centrifuged material was mixed on a Unimax mill and dried at 60° C in a circulating-air drying oven. Maintenance of this drying temperature and of the drying times was given particular attention to avoid further, uncontrollable breakdown during drying.

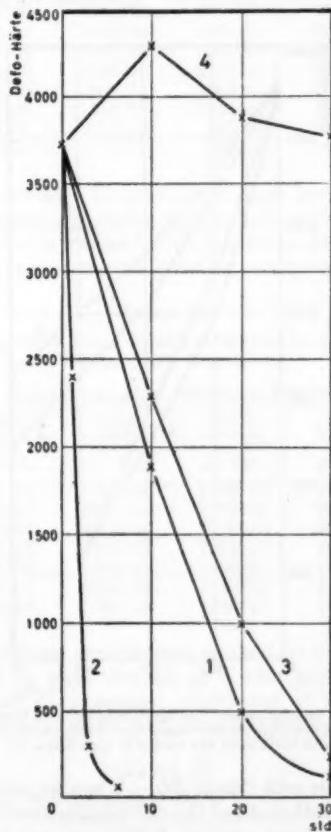


FIG. 5.—Dependence of Defo hardness on heating period at 120° C. Notation of curves: 1, latex with 0.0023% Co (in relation to solid rubber)—3 atm air; 2, same latex and Co—3 atm O₂; 3, latex without Co—3 atm air; 4, latex without Co—3 atm N₂.

Softening³ with cobalt naphthenate.—The first experiments were conducted with cobalt naphthenate as an oxygen transfer agent, using 0.0023 per cent cobalt with reference to the solid rubber. In some individual experiments a fivefold dose was used. The experiments permitted the following observations: The rate of breakdown is a function of temperature (experiments KH 29, 42, 52). The higher the temperature, the faster the breakdown proceeds. From Experiments 31, 40, 41, 42, 46, 49 and 48 it can be seen that the oxygen partial pressure in the air likewise influences the rate of breakdown. A five-

fold increase in the amount of cobalt (Experiments 37 and 38) causes only a minor change in the rate of breakdown. Omitting the oxidation catalyst (Experiments 46 to 51) also leads to breakdown, but the rate is sharply reduced. The results presented in Table I (which is omitted from this translation) and Figures 4, 5, and 6 were obtained by introducing the air or nitrogen-oxygen mixture into the latex under pressure. Bubbling through the latex did not take place.

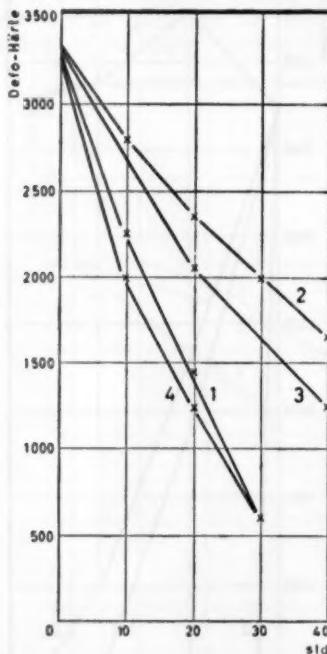


FIG. 6.—Defo hardness as a function of the heating time at 80° C. Notation of curves: 1, latex with 0.0023% on dry rubber of Co—3 atm O₂; 2, latex without Co—3 atm O₂; 3, latex with 0.0023% on dry rubber of Co—3 atm N₂; 4, latex with 0.012% on dry rubber of Co—3 atm O₂.

Softening^a experiments with Citosic RO.—When we resumed our experiments there was no cobalt naphthenate of the old quality available. For this reason we substituted, as breakdown catalyst, 0.0023 per cent of mixed metals as the naphthenate, "Citosic RO", which had approximately the following metal concentration:

1.40%	lead
0.5%	cobalt
0.1%	manganese
0.02%	iron
0.2-0.3%	calcium

As can be seen from Table II, the rates of softening are sharply curtailed in comparison with the higher cobalt-content naphthenate. Table III shows that the speed of reaction, when the metal content is 0.0012 per cent in relation to the dry rubber, is still quite low, whereas this speed increases when the quantity

TABLE II

SOFTENING EXPERIMENTS WITH THE METAL NAPHTHENATE, CITOSIC RO

Period of treatment at 3 atm gage air press., hours	Enamelled pot H2269	Enamelled pot H2272	"Remanit" pot H2275	Enamelled pot H2277	Enamelled pot H2278
	80° C raw Defo	90° C raw Defo	100° C raw Defo	100° C raw Defo	100° C raw Defo
0	3500/44	3900/44	3900/44	3900/44	3900/44
5	2700/44	2550/43	2650/45	2400/44	2900/43
10	2200/43	2000/42	2300/44	2300/44	2600/43
15	1800/40	1800/41	1850/43	2050/43	2350/43
20	1600/38	1350/36	1450/40	1800/41	1800/42
25	1350/38	1200/33	850/36	1650/40	1400/38
30	1100/35	—	650/32	1500/39	1250/37

of metal is double or fourfold. In none of the cases, however, does it reach the favorable breakdown rates obtainable with cobalt naphthenate. However, a substantial acceleration was realized with this metal naphthenate when there was an increase in the oxygen partial pressure in the air (Table IV).

TABLE III

SOFTENING RATE WITH VARYING METAL NAPHTHENATE, CITOSIC RO, CONTENT

Treatment time at 3 atm gage air pressure, hours	Compound no., Metal content, and Temperature of treatment				
	H2269, 0.0023%, 80° C, raw Defo	H2271, 0.0046%, 80° C, raw Defo	H2277, 0.0023%, 100° C, raw Defo	H2278, 0.0023%, 100° C, raw Defo	H2279, 0.0012%, 100° C, raw Defo
0	3500/44	3500/44	3900/44	3900/44	3900/44
5	2700/44	2500/44	2400/44	2900/43	2800/44
10	2200/43	2100/44	2300/44	2600/43	2600/44
15	1800/40	1800/43	2050/43	2350/43	2350/43
20	1600/38	1500/42	1800/41	1800/42	1950/42
25	1350/38	1250/40	1650/40	1400/38	1850/41
30	1100/35	1200/38	1500/39	1250/37	1600/41

From the results of these experiments it could be inferred that when compressed air is allowed to pass through at 3 atm gage pressure at reaction temperatures of 80–100° C, a notable shortening of the breakdown periods should result. As already mentioned, the following softening experiments

TABLE IV

ACCELERATION OF THE SOFTENING RATE THROUGH INCREASE IN THE OXYGEN PARTIAL PRESSURE

Treatment time at 100° C 0.0023% metal, hours	Compound no., O ₂ pressure, and air pressure of treatment				
	H2278, 3 atm air, raw Defo	0.3 atm O ₂ , 2.7 atm air, raw Defo	0.3 atm O ₂ , 2.7 atm air, raw Defo	H2284 (IV), 1.2 atm O ₂ , air, raw Defo	H2284 (III), 1.2 atm O ₂ , air, raw Defo
				1.8 atm air, raw Defo	1.8 atm air, raw Defo
0	3900/44	2900/41	2900/41	3600/44	3600/44
10	2600/44	1500/39	—	—	1550/41
15	2350/43	—	—	—	1500/42
20	1800/42	1100/33	—	—	1100/34
25	1400/38	—	—	—	1025/36
30	1250/37	900/33	1200/38	I 475/23 II 475/26	850/32
40	—	850/32	—	—	525/24

were carried out in such a way that the compressed air was blown in through a tube whose lower end was perforated or equipped with a frit and was released via an excess pressure valve set at 3 atm gage pressure. The escaping air was measured with a gas meter. The quantity of air blown through is of no significance after it has passed a certain minimum amount. The individual experiments were highly reproducible. As can be seen from Table V, it was

TABLE V
INFLUENCE OF AIR BUBBLING ON THE RATE OF SOFTENING

Period of treatment at 100° C, 3 atm gage air pressure, hours	H2323, no addition, 100 l hr air bubbled through, raw Defo	H2277, 0.0023% metal, no air bubbling, raw Defo	H2287/V, 0.0023% metal, 40 l hr air bubbled through, raw Defo	H2285/II, 0.0023% metal, 92.5 l hr air bubbled through, raw Defo	H2287/II, 0.0023% metal, 121 l hr air bubbled through, raw Defo	H2287/III, 0.0023% metal, 145 l hr air bubbled through, raw Defo
0	3400/44	3900/44	3600/42	3600/44	3600/42	3600/42
10		2300/44	—	1150/36	—	—
15		2050/43	600/24	750/30	—	—
20	1250/37	1800/43	375/14	450/17	600/23	500/24
25		1650/40	280/10	310/14	450/17	—
30		1500/39	220/6	210/11	300/10	—
35		—	—	—	200/6	—
40		—	—	100/2	—	—

possible to break down a Buna S3 latex whose rubber possessed a raw Defo value of 3600, to a raw Defo value of 450 (Experiment H 2285/II) within 20 hours at 100° C and 3 atm excess air pressure, whereas breakdown without air bubbling, after 30 hours under the same conditions, had progressed to a raw Defo of only 1500 (Experiment H 2277). With this technical variant, softening in the latex now became possible at reaction rates justifiable from a technical production standpoint.

TABLE VI
SOFTENING EXPERIMENTS WITH ALKYL PHENOL

Treatment time at 100° C, 3 atm gage air pressure, approx. 100 l hr bubbled through, hours	H2323, without additive, raw Defo	H2285/II, 0.0023% metal, raw Defo	H2292, 0.2% alkyl phenol, raw Defo	H2287/IV, 0.1% alkyl phenol, raw Defo	H2322, 0.05% alkyl phenol, raw Defo	H2324, 0.10% alkyl phenol, raw Defo
0	3400/44	3600/44	4400/46	3600/42	3200/42	3500/44
10		1150/36	1450/39	—	1600/39	1900/43
15		750/30	1025/31	600/24	1300/40	1500/41
20	1250/37	450/17	625/22	375/14	1100/37	1000/34
25		310/14	—	280/10	—	—

Softening⁸ experiments with alkyl phenols.—All the softening experiments involving alkyl phenols were carried out with bubbling of compressed air at 3 atm gage pressure and a reaction temperature of 100° C. The alkyl chain (branched) of the alkyl phenols employed consisted of about eight carbon atoms. The proportion of added alkyl phenol, in relation to solid rubber, must be at least 0.1 per cent. From Table VI it is plain that adding 0.01 per cent and 0.05 per cent alkyl phenol is not sufficient to cause a noticeable speeding-up of breakdown in the latex, when compared to the experiment

without the catalyst. The values in Table VI demonstrate the dependence of the softening rate in the Buna S3 latex on the alkyl phenol concentration when air is bubbled through at 3 atm gage pressure, and also show the effect of Citosic RO and alkyl phenols when compared to an experiment without a catalyst.

Transition from alkyl phenol to substituted hydroquinone, e.g., ditertiary-butyl hydroquinone, also causes a certain hastening of breakdown, but the speeds attained will not be as high as those induced by using the alkyl phenol cited. Mercaptans and sulfur-containing phenols were also tested in several series of experiments, but did not effect any noteworthy acceleration of softening in the latex (see Table VII).

Practical application testing of Buna S3 rubber softened in the latex (see Table VIII).—For practical testing, two samples (H 2287/III and H 2284/IV) made from latex softened Buna S3 were selected together with a laboratory produced control sample of Buna S3 to be used as the 0-stage (H 2284C). The latter came from the same, but untreated, Buna S3 latex. Both latexes underwent breakdown in the presence of 0.0023 per cent metal content of a Citosic RO.

TABLE VII

INFLUENCE OF DIVERSE OXIDATION CATALYSTS ON RATE OF SOFTENING

Testing period at 100° C,		H2325, 0.1% dodecyl mercaptan, raw Defo	H2321, 0.1% dihydroxydi- phenyl- sulfide, raw Defo	H2321/II, initially 0.2% dihydroxyphenyl sulfide after 10 hrs 0.2% dihydroxydiphenyl- sulfide additive, raw Defo
3 atm gage air pressure, 100 l/hr air bubbled through, hours	H2323, no additive, raw Defo	3400/44 ↓ 1250/37	3500/44 2050/48 1600/46 1275/38	3000/40 1800/42 1800/44 1375/41
0				3500/44
10				3700/48
15				2400/47
20				2150/47

The H 2284 product was obtained after 40 hours at 100° and 3 atm gage pressure of oxygen-enriched air, and product H 2287 after 20 hours at 100° C and 3 atm gage air pressure, through use of the bubbling process. The 0-stage is always necessary for semitechnical experiments if a true comparison of the softened sample with the respective latex under consideration is to be secured. Generally it is not proper to compare these semitechnical test samples with the properties of a factory-produced batch of Buna S3. Nevertheless, for characterization purposes, a normal batch of Buna S3 (CD II/1011) is included in Table VIII, together with a production sample of Buna S4 (BD 2505). Table VIII contains test data of interest only in this connection, especially data for a vulcanizate highly loaded with black, and for the storage of the raw material at 36° C.

From the data for the vulcanizates of these products it is plain that tensile strengths, elongations at break and permanent sets, as well as rebound elasticities, Shore hardnesses and notch impact resistances show no essential differences, either among themselves or in comparison with normal Buna S3. The tensile level of the factory samples of Buna S3 and S4 is higher. This shows the necessity of using the control sample H 2284C as the 0-stage. The Buna S4 used for comparison has a rebound elasticity which lies some 5 to 7 points lower than that of products obtained from Buna S3 polymers including those softened in the latex. Storage of the Defo testpieces at 36° C, up to

TABLE VIII
RESULTS FOR BUNA S3 SUBJECTED TO SOFTENING IN THE LATEX

Sample	Pretreated, degrad-	Raw material plasticity**	Mixture 19 com-	Ten-	Elonga-	Re-	Im-	Raw Deto of raw material storage at 36° C., days				
								per-	ma-	nent	elast-	Shore
H2287/II	Citrosic, 20 hrs	450/24	1425/31	204	570	12	49	63	10.8	625/28	750/31	1050/37
H2284/IV	Citrosic, 40 hrs	475/26	1700/32	215	525	13	46	64	9.9	625/29	750/32	1100/38
H2284/C	0-stage	400/19	1275/29	211	515	11	47	65	8.0	525/24	675/27	1050/36
S3 CD II/1011	Normal Buna S3	450/21	1325/30	249	560	14	48	64	8.8	575/24	750/28	875/30
BD 2505	Normal Buna S4	500/28	1200/25	239	550	16	42	65	8.8	475/20	400/19	425/21

* Vulcanizate data for Compound 19, cured 60 min at 134° C.

** Including that obtained through thermal degradation, raw Deto.

72 days, revealed distinct differences in the behavior of Buna S4 materials as compared to those derived from Buna S3. After 72 days the latter showed an increase of Defo value of more than 50 per cent, whereas the Defo value of Buna S4 remained practically constant, i.e., Buna S4 stored up to 72 days exhibits no recovery characteristics. Figure 7 presents the relationship of Defo hardness to Defo elasticity in thermally softened and latex softened Buna S-3 polymers. The closely-grouped curves show that in this instance no fundamental differences are present.

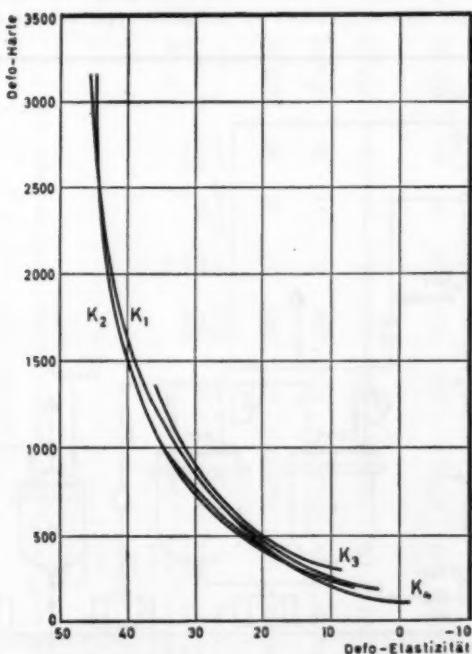


FIG. 7.—Defo hardness versus Defo elasticity values of thermally softened and latex softened Buna S3 polymers; K1 = H 2284, K2 = CD II 1152/409, K3 = H 2285/II A-F, and K4 = H 2286/II A-F. The Buna S3 was thermally softened for K1 and K2 and softened in the latex for K3 and K4.

PILOT PLANT EXPERIMENTS IN FLOW EQUIPMENT

Apparatus (Figure 8).—The apparatus consists essentially of an enameled cast iron countercurrent tube, having a diameter of 360 mm and a height of 4000 mm. It is divided into four sections and has a heating jacket for low pressure steam (b). By means of a pump, the latex to be used is pressure-forced from an enameled container (d) into the lowermost section of the countercurrent reaction apparatus. In the top section there is a spillway leading, selectively, to one of the two supply or stock vessels (c). The compressed air is forced through the latex in a finely dispersed form. The outgoing air is regulated by means of an overflow valve (e) and measured with a gas meter. The installation is equipped with a 3 atm excess pressure safety

valve and a sufficient number of temperature measurement points. With this apparatus approximately 250 liters of Buna S3 latex can undergo softening at once. It proved expedient, for the time being, to carry out the softening discontinuously, since the period of 30–40 hours (or, when large amounts of breakdown accelerators were used, of 15–20 hours) was too long, and premixing of the already broken down latex with fresh, unbroken down latex could not be avoided. As is well known, however, baffle plates can be built into this countercurrent tube so as to cause a laminar flow of the latex. With this apparatus softening tests were carried out principally with alkyl phenols, so that softened Buna S3 could also be subjected to application tests.

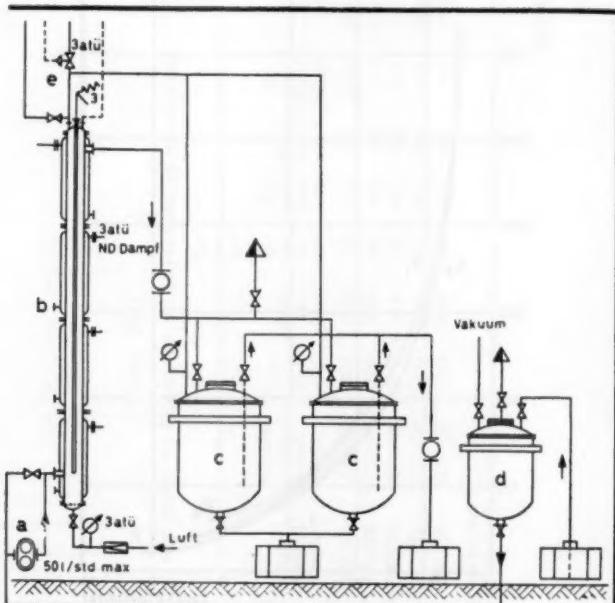


FIG. 8.—Flow apparatus.

Technical application test of the pilot plant latex softened products (Table IX).—In the practical experiments it was recognized that a large proportion of phenyl-2-naphthylamine has a favorable effect on the recovery of latex-softened Buna S3. Experiments with known storage-protective materials derived from aromatic amine-formaldehyde reaction products gave negative results, at least in application experiments. It is known also in thermal softening of Buna S3 that a portion of the phenyl-2-naphthylamine is lost through oxidation. For this reason the stabilization of Buna S3 with phenyl-2-naphthylamine was repeatedly measured and the necessary concentration found to occur between 2 and 3 per cent. In the preparation of the experimental products enumerated in Table IX, our procedure included therefore the addition to the latex, after breakdown but before precipitation, of more phenyl-2-naphthylamine as an aqueous suspension, up to the prescribed percentages.

TABLE IX
RESULTS OF PILOT PLANT-PREPARED LATEX-SOFTENED PRODUCTS

Test no.	Preparatory treatment	Raw material plasticity, after thermal softening	Phenyl-2-naph-thyl-amine content after softening, %	Storage of raw materials at 40° C		Shore hardness*	Re-bound*	Storage of raw materials at 40° C Raw Defo values after 16 days	48 days	96 days
				Compd. 19	Coupl. Defo					
GH122/Vb	Softened in latex, 100° C, 20 hrs	700/30	2.7	1650/36	177	565	14	46	60	850/32
GH122/VII	0-stage without degradation	750/29	2.0	1650/36	172	530	11	44	56	970/32
Buna S3	Thermal degra- dation	750/31	1.8	1950/36	216	540	11	45	64	950/32
GH122/III	Degradation in latex, 100° C, 17 hrs	900/35	1.3	1750/33	185	615	13	46	60	1025/35
										1300/40
										1410/38

* See footnote to Table VIII.

This action proved favorable, in the storage test at 40° C, as is evident from the figures provided in Table IX.

The product GH 122/III, with a phenyl-2-naphthylamine content of only 1.3 per cent on the solid rubber, toughens during storage up to 96 days more substantially than the product GH 122Vb, whose phenyl-2-naphthylamine content was 2.7 per cent. In this case, after a 96 day storage at 40° C, hardly any rise in Defo value was noticed. The 0-stage rubber of 750 Defo value tested along with it, whose phenyl-2-naphthylamine content was originally 2.8 per cent, but which fell to 2.0 per cent during breakdown, also showed strong recovery. The vulcanizate data for the latex softened products are at about the same level. The concurrently-tested Buna S3 factory sample also exhibited stronger recovery. The level of vulcanizate data is somewhat higher. This adequately proved that even when an alkyl phenol was used, the quality level remained as high as that achieved with metal naphthenates.

CONCLUSIONS

When butadiene copolymerization is modified, the polymers produced suffer a certain loss in some properties measured after compounding, especially in heavily-loaded compounds. This has been substantiated again in the mass production of Buna S4 and Buna NW. What is gained in the plasticity of Buna S4 as raw material is lost with regard to the elasticity of its black-filled compound. In the interests of preserving the quality level, it is better to first build up a polymer chain with long molecules and then modify it through thermal breakdown. The plant installation required for thermal softening is not inconsiderable, and is not available in all countries where rubber is processed.

The new softening process for Buna S3 latex in the presence of the previously-described oxidation catalysts, bringing the rubber to the plasticity level of a Buna S4, represents a certain enhancement and expansion of the production methods of the synthetic rubber industry because the thermo-oxidative plasticization in the latex not only ensures good processibility of the raw material, but preserves the high quality level of the original Buna S3, particularly the elasticity of heavily loaded compounds. It is possible to repress the so-called recovery of the latex softened product by careful dosage with phenyl-2-naphthylamine. Buna S4 produced by controlled polymerization, however, lies at a processibility level, especially in highly-filled compounds, that is not reached by materials softened in the latex to Buna S4.

The procedure is not limited to Buna S3. In exploratory experiments low temperature rubber with a raw Defo value of about 3000 in the latex was also plasticized to a raw Defo value of 600-800. Here the same advantages are in evidence as cited for Buna S3. The recovery of the material softened in the latex could be practically completely inhibited. With the present latex softening it has not as yet been possible to plasticize a Perbunan latex with a raw Defo level of about 3000.

To date the technical aspects of the described latex softening method have not been worked out completely. This is especially true of the countercurrent reaction tube. The latex softening time of some 20 hours seems quite feasible, technically speaking. By raising the oxygen content of the air used for oxidation, these periods can be further shortened. Since industrially produced Buna S3 latex still contains slight amounts of monomeric styrene, of the order 0.1 to 0.2 per cent, the introduction of the softening process involving air and oxygen-enriched air will require a more careful consideration of technological safety

factors, and more experimentation. Above all, the explosive limits of air-styrene mixtures at various pressures must be determined.

SUMMARY

A method is described for plasticizing Buna S3 when still as a latex. A plasticization of Buna S3 to the Buna S4 stage is carried out in the presence of metal sols or alkyl phenols, and through use of air or oxygen-enriched air. Softening takes place under low gage pressure, at temperatures around 100° C, and at rates that are technically feasible. In contrast to Buna S4 that has been produced soft by means of polymerization control, the Buna S4 obtained through this softening process has certain advantages, e.g., higher elasticity values in heavily-loaded compounds. So-called recovery can be retarded by careful dosing with phenyl-2-naphthylamine. The introduction of this process into the synthetic rubber industry, using continuous latex breakdown in a countercurrent reaction tube, is discussed.

ACKNOWLEDGMENT

The practical, industrial tests were in charge of H. Luttrupp. Dr. Grieshaber handled, among other things, softening in latex with alkyl phenols on a semitechnical scale. Mr. Richter carried out the technical experiments. Dr. Zaucker suggested experimentation with alkyl phenols. The author wishes to express his sincere appreciation to his colleagues for their cooperation.

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- ⁸ Translator's note: Softening was followed by K values. For a discussion of these see the various references in the subject index of "Synthetic Rubber" edited by Whistby. John Wiley and Sons, New York, 1954.

REACTIONS OF FREE RADICALS IN SOLUTION. V. DESTRUCTION OF POLYMERIC MOLECULES BY FREE RADICALS *

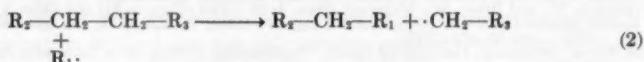
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The majority of the free radical reactions described in the literature are chemical conversions where the radical splits off a hydrogen or halide atom from the solvent¹.

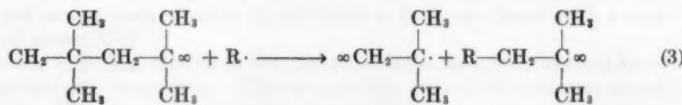


At the same time, similar reactions where a carbon-carbon bond in organic compounds is broken, have been studied in only a few cases. Thus, for example, Klebansky and Fomina established that the diallyl bond in complex organic molecules was broken by free radicals². Dolgoplosk, Tinyakova and Reikh established that oxidation-reduction systems, which are sources of free radicals, cause the destruction of polyisobutylene and other polymers in hydrocarbon media^{3,19}. It must be noted that such reactions were generally considered as very unlikely until lately, as in this case the radical attack occurs not through breaking of a bond as in (1), but internally as in (2):



In such a mechanism, the formation of a transition complex is hindered and the activation energy¹ of the process is increased.

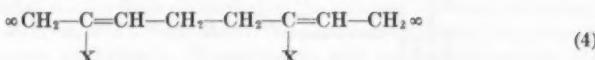
It was shown in a previous report² that free aliphatic and aromatic radicals ($CH_3\cdot$, $C_2H_5\cdot$, $C_6H_5\cdot$, $C_6H_5-C_6H_4\cdot$, etc.), formed by decomposition of corresponding diazoamino compounds, cause gel formation in concentrated benzene solutions of natural rubber. At the same time, a considerable decrease in viscosity is observed under analogous conditions in solutions of polyisobutylene, which does not have double bonds. This was explained by the reaction of the free radicals with a weak carbon-carbon bond by the following scheme:



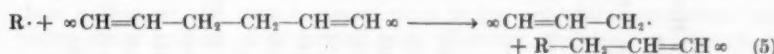
It seemed likely that this reaction is not specific for polyisobutylene but occurred in the case of any polymers with weak carbon-carbon bonds, for example, polymers of isoprene, divinyl and other dienes, containing diallyl

* Reprinted from the *Journal of General Chemistry (USSR)*, Vol. 26, pages 2461-2468 (1956); English translation of *Zhurnal Obshchey Khimii* 26, 2201-2209 (1956) by Consultants Bureau, Inc.

grouping of the atoms in the chain:

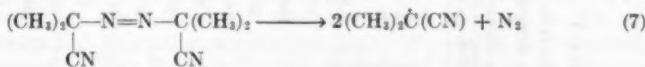


In this case the reaction of free radicals with the polymeric molecules would be expected to develop in two competing directions: a) "sewing together" of polymeric chains, resulting in an increase in the viscosity of the solution and in gel formation, and b) polymer degradation due to the breaking of carbon-carbon bonds:



Apparently, the proportion of the reaction leading to the buildup of the polymer must fall with a decrease in the concentration of the solution. While, on the contrary, the degree of degradation of polymeric chains, which is not due to intermolecular reactions of the latter, should appear in a more "pure" form in sufficiently dilute solutions.

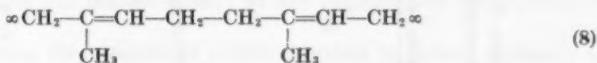
The reactions of some free radicals with polymers of different structure and over a wide range of concentrations were studied in the present work. Alkylphenyltriazene and azoisobutyronitrile, which decompose on heating to form alkyl and dimethylcyanomethyl radicals, were selected as sources of free radicals:



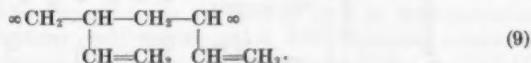
where $\text{alk}\cdot = \text{CH}_3\cdot$, $\text{CH}_2 = \text{CH}-\text{CH}_2\cdot$, $\text{C}_6\text{H}_5\text{CH}_2\cdot$.

As was established previously, these radicals, and likewise the radical $(\text{CH}_3)_2\dot{\text{C}}(\text{CN})$, differ markedly from each other in their reactivity in abstracting an H atom from organic compounds⁴.

Sulfur monochloride was also used in this work along with the radicals mentioned. It is known that sulfur monochloride is a strong agent for building up. The hypothesis has been put forward in the literature⁵ that the vulcanizing action of sulfur monochloride is due to the development of a radical type of reaction. In connection with this, it seemed interesting to study the action of sulfur monochloride in dilute polymer solutions. Natural rubber (NR) containing only units connected in the 1,4-position



synthetic polyisoprene (SPI), containing a considerable number (up to 90%) of units connected at 1,4 and polydivinyl rubber (SRB) with the majority of units connected at 1,2 (up to 70%).



were used for the study.

TABLE I
VISCOSITY OF BENZENE SOLUTIONS OF RUBBERS AFTER HEATING WITH DIAZAMINO COMPOUNDS (2 HOURS AT 100°),
AZOBISBUTYRONITRILE (1 HOUR AT 80°) AND SULFUR MONOCHLORIDE (5 HOURS AT 100°)

Natural rubber.		Reduced viscosity of the original solution $\eta_{red} = 12.05$		Synthetic polyisoprene. Reduced viscosity of the original solution. $\eta_{red} = 5.23$		Polydivinyl polymer SRB. Reduced viscosity of the original solution. $\eta_{red} = 5.23$							
R.	Pdr.	R.	Pdr.	R.	Pdr.	R.	Pdr.						
CH_3	5	1.83	{ 5	1.12	{ 20	0.80	{ 0.3	20	0.76	{ 0.3	5	1.72	
	1.0	1.04	21.0	20	1.05	100	1.37	1.0	2.40	1.0	5	2.95	
	2.0	0.71	{ 3.0	{ 5	1.68	{ 10	1.12	{ 50	2.41	{ 20	Gel		
	{ 10	2.63	{ (CH ₃) ₂ C(CN)	{ 20	1.30	{ 100	1.12	{ 5	2.82	{ 1	6.91		
	2.0	4.0	1.95	{ 5	1.46	{ 5	2.47	{ (CH ₃) ₂ C(CN)	3.0	{ 10	2.34		
	1.0	2.15	{ 20	1.37	{ 10	2.86	{ 3.0	30	2.17	{ 3.0	1	Gel	
	{ 2.0	2.94	{ 10.0	{ 5	2.56	{ CH ₃	{ 20	Gel	{ 3.80	{ 1.0	{ 20	3.92	
	{ 1.0	3.12	{ 0.5	{ 5	0.80	{ CH ₃	{ 100	Gel	{ 5.0	{ 5	{ 50	3.78	
	2.6	2.0	4.70	{ 1	5	0.61	{ 5	2.69	{ (CH ₃) ₂ C(CN)	{ 10	3.83		
	2.7	2.0	Gel	{ 2	5	0.65	{ 4.0	10	Gel	{ 0.5	{ 5	0.62	
S ₂ Cl ₂	3.0	1.0	Gel	{ 3	5	1.31	{ 40	Gel	{ 1	{ 5	0.78		
	5.0	1.0	Gel	{ 4	5	1.72	{ 5	4.48	{ SrCl ₂	{ 2	{ 5	1.66	
	{ 5	0.59	{ C ₆ H ₅ CH ₃	{ 0.5	5	11.73	{ 5.0	10	Gel	{ 3	{ 5	2.25	
	{ 50	0.51	{ CH ₃ =CH—CH ₃	{ 0.5	5	12.23	{ 40	Gel	{ 4	{ 5	Gel	2.0	
	{ 50	0.51	{ CH ₃ =CH—CH ₃	{ 0.5	5	12.23	{ 40	Gel	{ 5	{ 5	Gel	2.0	

The experimental results from determining the reduced viscosity of benzene solutions of these rubbers when heated with the above compounds, in a nitrogen atmosphere, are given in Table I. Experiments with azoisobutyronitrile (D) were carried out at 80° and those with methylphenyltriazene (M) and S_2Cl_2 at 100°. Heating was continued for 5 hours in the case of S_2Cl_2 and 1 to 2 hours for the rest. The above differences in experimental conditions were due to the different decomposition kinetics of the initiators.

The data obtained confirm the above hypothesis on the existence of two competing directions of the reaction of free radicals with polymers. All three rubber samples were degraded when in low concentrations, while with higher concentrations, they formed gels. However, the reaction intensity in both cases depends substantially on the polymer structure and the activity of the free radicals.

First of all, it should be noted that radicals of such low activity as benzyl and allyl, which are incapable of reactions breaking a C—H bond⁴, remained ineffective even in breaking a carbon-carbon bond. The more active methyl radical caused gel formation in NR and SPI at concentrations of 2.7–3.0 per cent and above, while at lower concentrations it caused degradation. Gel formation was observed in the case of SRB rubber at a polymer concentration of only 1.0 per cent, as this rubber is characterized by a large number of vinyl groups in the chain. This agrees with the known capacity of side vinyl groups to add free radicals readily⁶. The fact that SRB has little tendency to be destroyed may be due to the insignificant number of diallyl units with weak carbon-carbon bonds in the polymer chain of this rubber. The radical $(CH_3)_2\dot{C}(CN)$, which has relatively low activity, did not produce gel formation in NR and SPI even at very high polymer concentrations (up to 10 per cent) but invariably caused destruction. This is due to the low capacity of inner double bonds in a polymer chain to add free radicals of low activity. At certain polymer concentrations this radical does produce gel formation with SRB rubber, which contains a large number of side vinyl groups. The high reactivity of outer double bonds (vinyl groups) with $(CH_3)_2\dot{C}(CN)$ had been indirectly established earlier during the investigation of the products of reaction of this radical with olefins.⁷

The behavior of sulfur monochloride seemed especially interesting. When a solution of S_2Cl_2 was introduced at room temperature into a rubber solution, regardless of concentration, the solution gelled. However, when the solution was then heated, the gel disappeared and the solution viscosity decreased to the value given in Table I. Only in certain cases (polyisoprene and SRB) at high concentrations did the gel formed at the beginning of the experiment not disappear.

Besides studying the viscosity of rubber solutions it seemed necessary to determine directly the mean molecular weight of the original rubber and samples subjected to free radical action, as an explanation for the decrease in rubber solution viscosity could perhaps have been found without recourse to the idea of polymer chain destruction, as for example, by considering the formation of rigid globules impervious to the solvent (due to intramolecular macromolecule vulcanization), and having other hydrodynamic constants. For this purpose two solutions of natural rubber in benzene (NR-I and NR-II) were prepared and heated with azoisobutyronitrile (D), methylphenyltriazene (M) and sulfur monochloride. The molecular weight M was measured by

using an ultracentrifuge. As is known⁸:

$$M = \frac{S_0}{D_0} \cdot \frac{R \cdot T}{1 - V \cdot \rho} \quad (10)$$

where S_0 and D_0 are sedimentation and diffusion constants, R is the universal gas constant, T the absolute temperature, V , the partial specific volume of the dissolved polymer and ρ , the solvent density. Octane was used as solvent in experiments for determining S_0 and D_0 . The rubbers were transferred directly from the benzene solution into octane without precipitation, by the gradual change of the solvent⁹. The sedimentation constant S_0 was calculated by extrapolation to infinite dilution using the equation:

$$\frac{1}{S} = \frac{1}{S_0} + k''C \quad (11)$$

which gives satisfactory results at sufficiently high dilutions¹⁰. The values of the sedimentation coefficients S were determined by the shift in the maximum in the sedimentation diagram, obtained by Svensson's optical method¹¹. With the usual corrections, the value S was reduced to 20° and 1 atm¹².

The diffusion coefficient D was determined for all samples at a starting concentration of 2–2.5 mg/ml with Lamb's apparatus, fitted with an optical scale, a thermoregulator ($\pm 0.003^\circ$) and an automatic device for photographing the scale. For calculating the molecular weight we used the coefficient D_A computed by the method of ordinates and planes, as this gives results which correlate better with data for narrow fractions¹³. Concentration effects were excluded by the Boltzmann-Gralen method¹⁴ by the asymmetry of the diffusion diagrams. Practically, this procedure was needed only in the case of original rubber samples as deviation from symmetry of the destroyed samples was within the limits of accuracy of the measurement (2–3 per cent). Special control experiments confirmed the adequacy of such a procedure. The value D_A was also reduced to 20°. According to our measurements the ratio $(R \cdot T / 1 - V \cdot \rho)$ was equal to $9.18 \cdot 10^{10}$ for isoprene rubber in octane.

The molecular weight calculated by this method using formula (10) was close to the most probable (i.e., corresponding to the maximum of the weight distribution) weight M_m .

Inverse values of the sedimentation coefficients $(10/S)$ as functions of concentration are shown in Figure 1 for a number of samples. Results of the measurements are given in Table II. The average error in the determination of S_0 and D_0 was not more than 4–5 per cent.

Thus, there is an indisputable and, furthermore, very strong destruction effect caused by the free radicals. The similarity of the M_m values obtained for all destroyed samples and especially the fact that the same results were obtained for both samples in the case of S_2Cl_2 , indicate that the decomposition of the chains was of a random character, with equal probability of breakage in any of the monomer links.

As was shown independently by Durup¹⁴ and Charlesby¹⁵, after the third or fourth break all traces of the original distribution are lost and the resulting molecular-weight distribution approaches a Poisson distribution, with the same parameter values, regardless of the previous history of the sample.

As an independent control, the osmotic pressure π of four samples of the

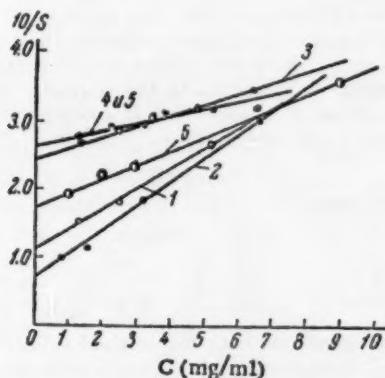


FIG. 1.—The relation of sedimentation coefficients to concentration for NR-I and NR-II in octane.
1) NR-I, 2) NR-II, 3) NR-II + M, 4) NR-I + S₂Cl₂, 5) NR-II + S₂Cl₂, 6) NR-I + D(a).

NR-II series was measured at the same concentration (9.1 mg/ml). Benzene with equal portions of dissolved *M*, *D* and S₂Cl₂ was used as solvent. As the difference in the levels in osmometry is inversely proportional to *M* (an average molecular weight is obtained here which is substantially lower than the most probable) then the results given in Table III are well correlated with the original data.

Besides this, it was interesting to find out whether intramolecular sewing together in the macromolecules was occurring parallel with the destruction. With this in mind an evaluation of the effective macromolecular dimensions was carried out based on the theory of Kirkwood-Riseman¹⁶ and Mandelkern-Flory¹⁷. Combination of the basic equations of these theories results in the equation:

$$F = 5.1 \langle r^2 \rangle^{\frac{1}{2}} \quad (12)$$

where: $F = (M/S_0) (1 - V \cdot \rho) \cdot N$ (N = Avogadro's number) or $R \cdot T / D_0 N$ is the friction coefficient of one macromolecule. Substitution of the appropriate values in (12) gives $\langle r^2 \rangle^{\frac{1}{2}} = (M/S_0) \cdot 9.83 \cdot 10^{-24}$ cm (see the last column in Table II) for the mean square of the distance between the ends of the molecule.

As is known, $\langle r^2 \rangle^{\frac{1}{2}}$ increases in nonideal solvents, due to volume effects¹⁸, with an increase in molecular weight proportional not to $M^{\frac{1}{2}}$ but to M^a , where: $1 > a > 0.5$ ($\langle r^2 \rangle^{\frac{1}{2}} = KM^a$). In this case *K* and "a" are characteristic

TABLE II
RESULTS OF MOLECULAR WEIGHT (M_m) MEASUREMENTS
FOR NATURAL RUBBER SAMPLES

Substance	$S_2 \cdot 10^{24}$	$(D_A)_0 \cdot 10^7$	$M_m \cdot 10^{-4}$	$\langle r^2 \rangle^{\frac{1}{2}} / A$
NR-I	9.09	1.65	614	664
NR-I + <i>D</i> (a)	5.71	3.38	155	212
NR-I + <i>D</i> (b)	5.88	4.37	127	267
NR-I + S ₂ Cl ₂	3.85	6.33	56	143
NR-II	14.7	1.07	1263	844
NR-II + <i>D</i>	4.26	5.22	75	173
NR-II + <i>M</i>	4.13	5.66	67	159
NR-II + S ₂ Cl ₂	3.85	6.33	56	143

parameters for polymer homologs in the given solvent. If the specific hydrodynamic volume of the destroyed macromolecules decreased, due to intramolecular sewing together, then the values of the parameters K and " a " would change accordingly (in relation to the original). Therefore, the construction of a graph of $\log \langle r^2 \rangle^{1/2}$ against $\log M$ (see Figure 2) should give the answer to the question under consideration.

TABLE III

RESULTS OF DETERMINATION OF THE OSMOTIC PRESSURE OF SOLUTIONS

Height of column (in mm)	NR-II	NR-II+D	NR-II+M	NR-II+S ₂ Cl ₂
Outer capillary	0.5	9.0	18.0	11.2
Inner capillary	20.0	72.0	78.5	68.0
Difference in level	19.5	63.0	60.5	56.8

The experimental points for both the original rubber and the destroyed samples fall very well in one straight line corresponding to the equation:

$$\langle r^2 \rangle^{1/2} = K \cdot M^{0.647} \quad (13)$$

The value of the index " a " (0.620) was very close to that found earlier for synthetic polyisoprene rubber. Thus, the values of the parameters K and " a " do not change during the degradation of natural rubber. This provides a sufficient basis for considering that no intramolecular chain vulcanization occurs during this process.

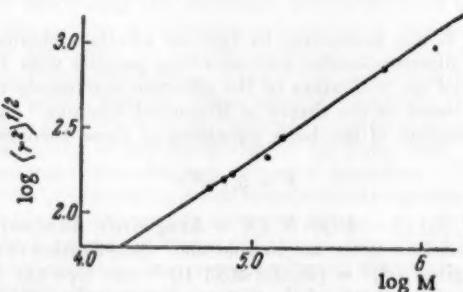
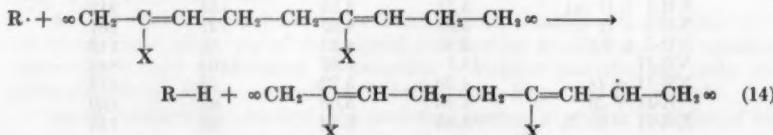


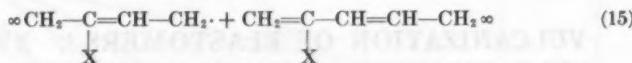
FIG. 2.—The relation of the mean square of the distance between the ends of the molecule to molecular weight for the samples NR-II, NR-II + M; NR-II + D, NR-II + S₂Cl₂.

The hypothesis based on Equation (5), of the reaction of free radicals with weak carbon-carbon bonds, is in accordance with experimental results; however, on the basis of the ideas expressed by Semenov¹, on the greater probability of Scheme (1) rather than Scheme (2), the mechanism of this reaction could be considered as proceeding in two stages:

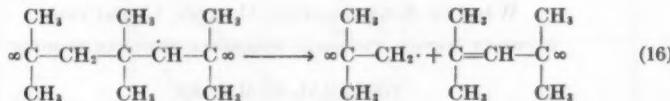
1) abstraction of an H atom from the polymer chain with the formation of a polymer radical:



2) decomposition of the polymer radical to form a diene grouping at the end of the chain and an allyl radical:



Such considerations appear less applicable to polyisobutylene destruction, as in this case the decomposition is accompanied by the formation of a more active primary polymer radical:



Only on the basis of a detailed investigation of the process on model systems could the problem of the mechanism of the elementary act in this process be solved.

It follows from the results of this work that in the process of polymerization it is necessary to allow for the development of destructive processes in which active centers and polymer radicals take part.

SUMMARY

1. It was established that free radicals produce degradation of polymer chains.
2. Ideas were put forward on the possible mechanism of the reaction leading to the breaking of a carbon-carbon bond in polymer molecules.

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VULCANIZATION OF ELASTOMERS¹. XV. THE VULCANIZATION OF NATURAL AND SYNTHETIC RUBBER WITH SULFUR IN PRESENCE OF ORGANIC BASES (I) *

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GENERAL SUMMARY

The results obtained from preliminary kinetic studies of the vulcanization of natural rubber (NR) with sulfur in the presence of organic bases may be summarized as follows.

- 1) The change of concentration of sulfur with time during reaction with NR for an initial sulfur concentration of 2.5 g per 100 g of mixture follows a fractional reaction order, n , of 0.6 at all temperatures. This result and the findings of other authors suggest that the reaction of sulfur with rubber is autocatalytic. From the temperature dependence of the rate constant the activation energy is found to be 35.3 kcal.
- 2) In the presence of zinc oxide and with a similar initial sulfur concentration, the reaction is first order and the activation energy, namely 35.6 kcal, is practically the same.
- 3) In the presence of diphenylguanidine (DPG) during cure sulfur decrease is a reaction of fractional order, $n = 0.75$, and the activation energy is 29.8 kcal.
- 4) For a given initial concentration of sulfur and at constant temperature the rate of sulfur decrease during vulcanization increases with rising DPG content and reaches a limiting value; i.e., the rate constant depends on DPG concentration. Also, for various base (DPG is basic) concentrations sulfur decrease is of various fractional orders, $n = 0.5 \dots 0.7$, etc.
- 5) The influence of base on the rate of sulfur decrease is interpreted broadly as a case of intermediate-catalysis (Zwischenstoff-Katalyse).
- 6) Vulcanization with sulfur is unaffected by tertiary amines and secondary amines have only a slight effect.
- 7) Primary amines, depending on basic strength, are strong accelerators of the rate of sulfur decrease.
- 8) In the presence of organic bases (aromatic amines) other than DPG, sulfur decrease is of fractional order where n varies between 0.5 and 0.7.

RESULTS AND DISCUSSION

The kinetics of the reaction of sulfur with natural rubber with and without zinc oxide.—The reaction of NR with sulfur alone² was investigated over the range of 115–150° C at an initial sulfur concentration of 2.5 g in 100 g of the mixture, corresponding to 0.98 mole of S₈ per 10 kg of mixture. The results are represented in Figure 1 (linear plot) and in Figure 2 (semilog plot). It

* Translated and abridged by Frans Widmer for RUBBER CHEMISTRY & TECHNOLOGY from an article in Kautschuk und Gummi 10, WT 185–194, August 1957. Tables I, III, IV, V, VI, VIII and X were omitted.

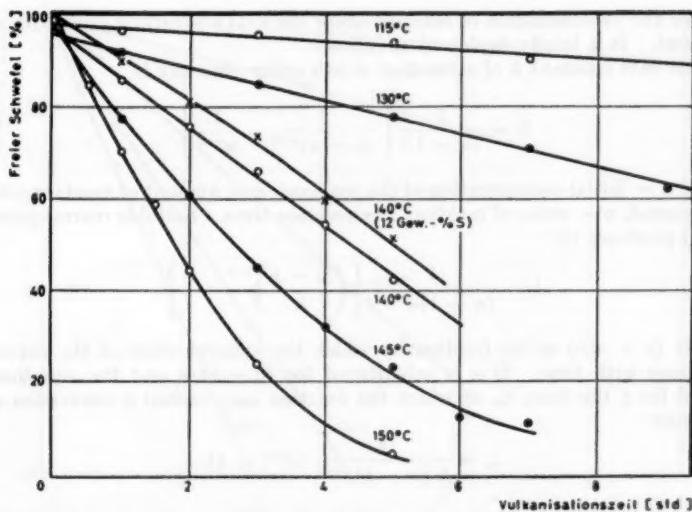


FIG. 1.—Decrease of the sulfur concentration with time during reaction with NR at various temperatures (2.5 g of sulfur per 100 g of mixture = 0.98 ~ 1 mole of S₈ per 10 kg).

can be observed that none of the plots produce straight lines. Therefore, it must be concluded that the reaction is neither zero nor first order but rather it is fractional order. The apparently straight lines which represent the reaction at low temperatures are no exception since the curvatures are not visible then because the reaction is so very slow.

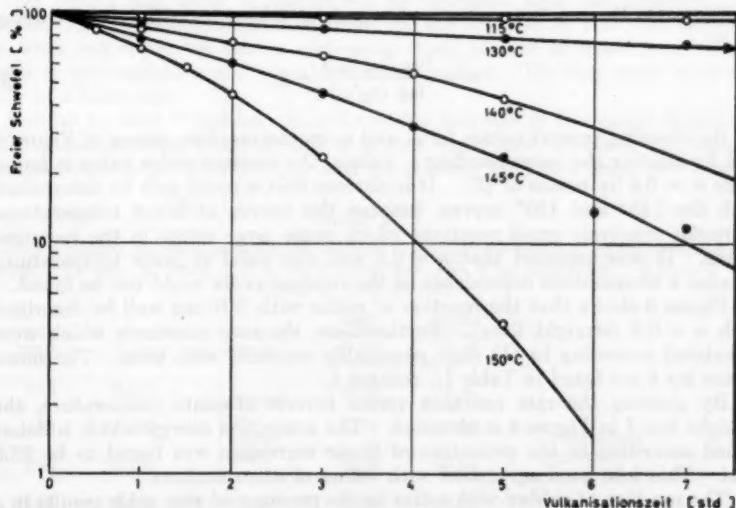


FIG. 2.—Semilogarithmic plot of the data for Figure 1.

For the determination of reaction order Ostwald's isolation⁸ procedure was followed. It is briefly explained as follows:

The rate constant k of a reaction of n th order generally is

$$k = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] \quad (1)$$

where a = initial concentration of the reactant, x = amount of reactant which has reacted, n = order of reaction, t = reaction time. Suitable rearrangement of (1) produces (2)

$$k = \frac{1}{(n-1)a^{n-1}t} \left[\left(\frac{a-x}{a} \right)^{1-n} - 1 \right] \quad (2)$$

In (2) $(a-x)/a$ is the fraction by which the concentration of the reactant decreases with time. If α is substituted for $(a-x)/a$ and the equation is solved for t , the time, t_α , at which the reaction has reached a conversion α is obtained:

$$t_\alpha = \frac{1}{k(n-1)a^{n-1}} (\alpha^{1-n} - 1) \quad (3)$$

If on any reaction curve two sufficiently different concentrations of the reactant $(a-x_1) = c_1$ and $(a-x_2) = c_2$ are chosen, the time values t_{α_1} and t_{α_2} can be read at which the concentrations c_1 and c_2 have decreased to an arbitrarily chosen, but in both cases equal, fraction α . From (3) the quotient $t_{\alpha_1}/t_{\alpha_2}$ is obtained to give (4).

$$\frac{t_{\alpha_1}}{t_{\alpha_2}} = (c_2/c_1)^{n-1} \quad (4)$$

From (4) the reaction order is obtained by taking logarithms and solving for n :

$$n = \frac{\log(t_{\alpha_1}/t_{\alpha_2})}{\log(c_2/c_1)} + 1 \quad (5)$$

By choosing several values for c_1 and c_2 on the reaction curves of Figure 1 and by reading the corresponding t_α values, the reaction order value is found to be $n = 0.6$ by means of (5). It is obvious that n could only be determined with the 145° and 150° curves, because the curves at lower temperatures represent relatively small reactions which cause large errors in the measurements. It was assumed that $n = 0.6$ was also valid at lower temperatures because a temperature dependence of the reaction order could not be found.

Figure 3 shows that the reaction of sulfur with NR can well be described with $n = 0.6$ (straight lines). Furthermore, the rate constants which were calculated according to (1) were reasonably constant with time. The mean values for k are listed in Table II, column 4.

By plotting the rate constant versus inverse absolute temperature, the straight line I in Figure 4 is obtained. The activation energy which is determined according to the procedure of linear regression was found to be 35.3 kcal. This is in good agreement with values of other authors.

The reaction of rubber with sulfur in the presence of zinc oxide results in a somewhat different relationship. Here the reaction is exactly of first order.

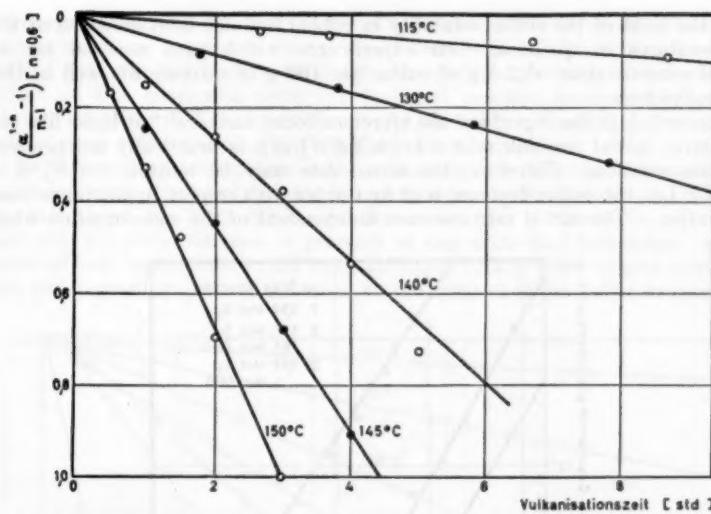


FIG. 3.—Decrease of sulfur concentration according to a reaction order, $n = 0.6$, during the reaction with NR at various temperatures (initial sulfur concentration ~ 1 mole of S_8 per 10 kg of mixture).

The decrease of sulfur concentration at various temperatures with time is represented in Figure 5 (see Table IV for starting composition). The temperature dependence of the rate constant is given by line II in Figure 4. The activation energy of 35.6 kcal is essentially that for the reaction in the absence of zinc oxide.

Our results and those of others will be discussed with the objective of determining the fractional reaction order for the reaction of NR with sulfur. Our work has suggested that a systematic study should be made over wide ranges of concentration and time by a single author. We may make such a study at a later date.

Results to date⁴⁻¹¹ indicate that the sulfur decrease in the range of small initial concentrations tends to follow a first order law, whereas, at initial concentrations larger than five per cent the reaction is of zero order providing

TABLE II

REACTION ORDER, RATE CONSTANT AND ACTION CONSTANT OF THE REACTION OF SULFUR WITH NATURAL RUBBER (2.5 G OF SULFUR PER 100 G OF MIXTURE = 0.98 ~ 1 MOLE S PER 10 KG)

Vulc. temp., $^{\circ}\text{C}$,	$\frac{1}{\text{K}} \cdot 10^4$	Reaction order, n	Rate constant $k \cdot 10^3$ for $n = 0.6$	Action constant $\log H$ for $n = 0.6$	
115	2.577	cannot be calcu- lated	0.16	16.10	
130	2.480		0.72	16.00	
140	2.421		2.30	16.04	Activation energy $Q_A = 35.3$ kcal
145	2.391	0.6	3.78	16.03	
150	2.363	0.6	5.69	16.00	

that the limit of the sulfur solubility in rubber has not been exceeded at the temperatures in question. Our experiments which gave $n = 0.6$ for an initial concentration of 2.5 g of sulfur per 100 g of mixture fits well in this general picture.

According to the reports of the aforementioned authors⁴⁻¹¹ it looks like the "relative" initial reaction rate $-1/[S_0][d[S]/dt]_0$ is practically independent of concentration. Therefore, the initial rate may be written $-d[S]/dt = k \cdot [S_0]$; i.e., the sulfur decrease is of first order with respect to any initial concentration. The initial rate becomes independent of the concentration when

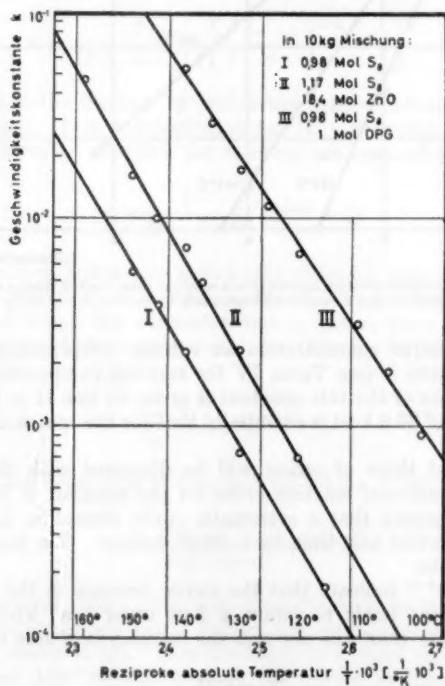


FIG. 4.—Temperature function of the rate constant for sulfur decrease; I, reaction of sulfur with NR without additives; II, reaction of sulfur with NR in presence of zinc oxide; III, vulcanisation of NR with sulfur in presence of DPG (1 mole of base and 1 mole of S_8 per 10 kg of mixture).

the solubility limit of sulfur in rubber at various temperatures¹² has been reached or exceeded. In these cases the sulfur decrease is of zero order also with respect to the initial rate. This situation was confirmed on the example of a sulfur cure at 140° with 12 g of sulfur per 100 g of mixture. The "relative" initial rate was the same as that observed with 2.5 g of sulfur per 100 g of mixture at the same temperature.

At this point the results are as follows: The reaction order lies between one and zero depending upon the initial concentration. The initial reaction rate, however, is of first order and it deviates soon after the initiation to become of fractional order. It is suggested that the nature of the sulfur decrease is a first

order reaction and the observed fractional reaction order is the result of circumstances which are created in the course of the reaction. Therefore, it seems possible that the sulfur decrease is an autocatalytic process. Van Iterson¹³ arrived at this conclusion from the S-shaped reaction curves which were obtained by Glancy, Wright and Oon,¹⁴ and Skellon¹⁵. The initial concentrations of these authors obviously were higher than ours.

An explanation of the nature of the autocatalysis is difficult. The possible creation of atom groups containing SH groupings may be considered, perhaps also radicals of the form HS_2^+ . In this connection it should be repeated again that the sulfur decrease in presence of zinc oxide is of first order. As a matter of fact, mercaptans would be transformed by zinc oxide to give mercaptides which possibly exert no influence on the kinetics of the sulfur decrease.

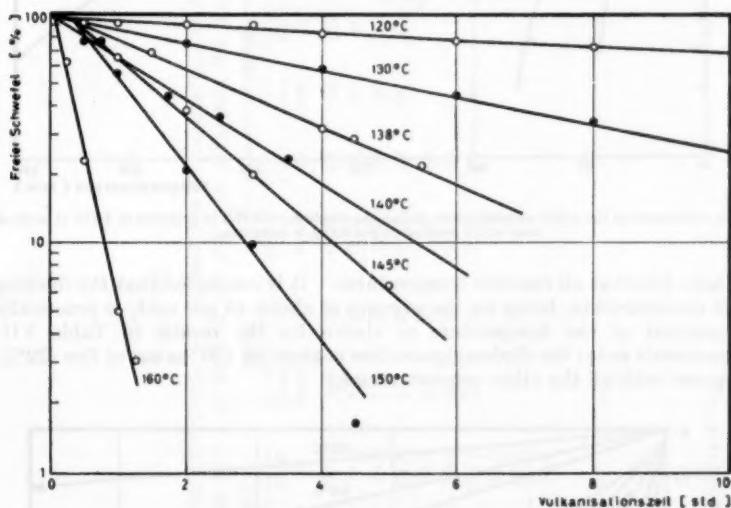


FIG. 5.—Decrease of the sulfur concentration during the reaction with NR in presence of zinc oxide (first order reaction).

Kinetics of the vulcanization of rubber with sulfur in presence of diphenylguanidine in dependence on the temperature.—It is well known that organic bases accelerate the sulfur cure of rubber, especially DPG and some other guanidine derivatives which are frequently used. Figure 6 consists of rate curves for the vulcanization of rubber mixtures which contained initially 2.5 g of sulfur and 2.0 g of DPG per 100 g of mixture (molar ratio of the additives $\sim 1:1$). The reaction order n is 0.75. By using $n = 0.75$ a family of straight lines was obtained as shown by Figure 7. The dependence of the rate constant k on temperature is represented by Curve III in Figure 4. Here it is clearly shown that the rate of sulfur decrease is considerably increased by bases.

Simultaneously with the decrease in sulfur concentration during the reaction, a decrease in DPG concentration occurs. After a rapid initial DPG decrease the rate of decrease levels off and the final DPG concentration remains practically constant over a wide range of the reaction time. This behavior

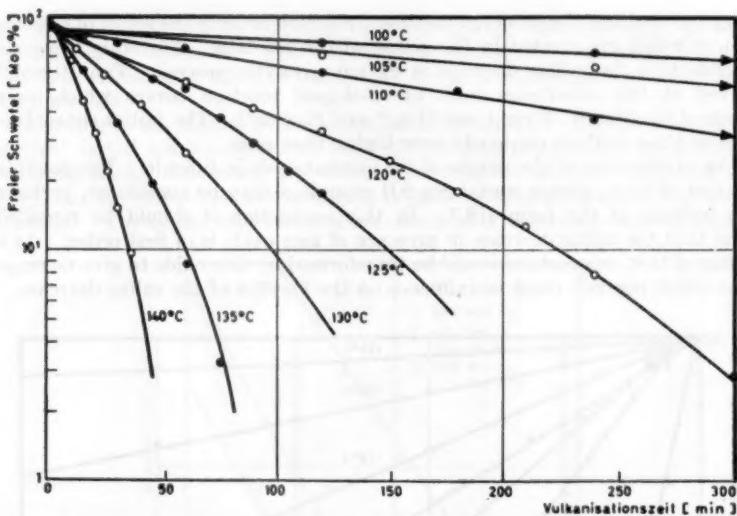


FIG. 6.—Decrease of the sulfur concentration during the reaction with NR in presence of DPG (1 mole of base and 1 mole of S₈ per 10 kg of mixture).

has been found at all reaction temperatures. It is concluded that the limiting DPG concentration, being on the average of about 45 per cent, is practically independent of the temperature as shown by the results in Table VII. (Translator's note: the diphenylguanidine content at 120° is out of line (22%) compared with all the other concentrations.)

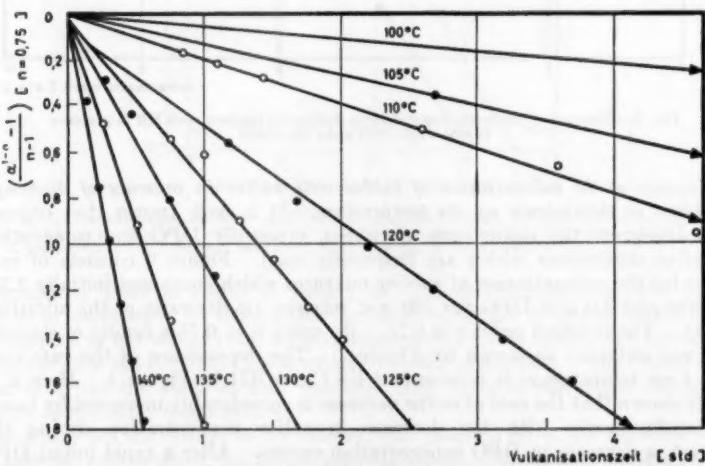


FIG. 7.—Decrease of the sulfur concentration according to a reaction order, $n = 0.75$, during the reaction with NR at various temperatures (1 mole of base and 1 mole of S₈ per 10 kg of mixture).

TABLE VII
DECREASE OF THE DIPHENYLGUANIDINE (DPG) CONCENTRATION DURING THE VULCANIZATION OF NATURAL RUBBER WITH SULFUR

AT VARIOUS TEMPERATURES (2.5 G OF SULFUR AND 2.0 G OF DPG PER 100 G OF MIXTURE)															
100° C		105° C		110° C		120° C		125° C		130° C		135° C		140° C	
Time, hours	DPG, %	Time, hours	DPG, %	Time, min.	DPG, %	Time, hours	DPG, %	Time, hours	DPG, %	Time, hours	DPG, %	Time, min.	DPG, %	Time, min.	DPG, %
2.0	51.0	2.0	49	0	79.0	1.0	50	0.50	43	12	40	15	44	10	45
4.0	50.0	6.0	49	3	77.0	1.5	22	0.75	43	24	40	30	40	15	44
6.0	47.0	10.0	48	6	73.0	2.0	22	1.00	42	40	39	45	—	20	46
8.0	46.0			15	67.0	2.5	20	1.25	45	60	41	60	47	25	47
10.0	47.0			30	56.0	3.0	21	1.50	45		45	—	30	46	44
12.0	47.0			60	56.0	3.5	21	1.75	43		90	45	35	47	36.0
14.0	47.6			120	56.0	5.0	20	2.00	44						59.0

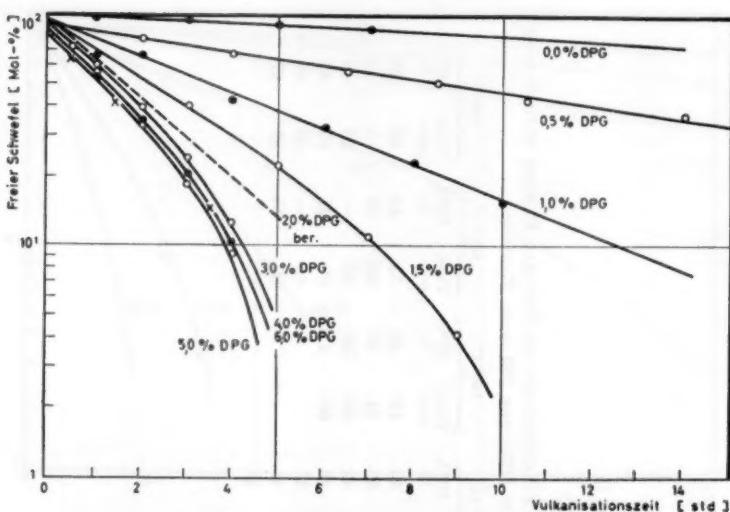


FIG. 8.—Decrease of the sulfur concentration during the reaction with NR in presence of various amounts of DPG at 115° C (~1 mole of S₈ per 10 kg of mixture).

The kinetics of the vulcanization. Dependence on DPG concentration.—The following series of experiments was run at 115° with a constant initial sulfur concentration of 2.5 g per 100 g of mixture. The DPG concentration was varied and increased up to 6 g per 100 g of mixture. The results are shown in Figure 8. With less than 1.5 per cent DPG the bend in the reaction curves is not visible, but at higher concentrations it is obvious. It must be concluded that DPG does not influence the fractional reaction order for sulfur decrease. The reaction order was found to be 0.5 to 0.7 (compare Table IX, column 3).

The reaction rate increases rapidly up to 3 per cent DPG concentration and then remains practically unchanged. Figure 9 illustrates this clearly.

Table IX shows that the nonextractable base in mole per cent decreases

TABLE IX

RATE CONSTANT OF THE SULFUR DECREASE AND AMOUNTS OF BOUND DIPHENYLGUANIDINE (DPG) DURING THE VULCANIZATION OF NATURAL RUBBER AT 115° C AS A FUNCTION OF THE DPG CONCENTRATION (0.98 ~ 1 MOLE OF S₈ PER 10 KG OF MIXTURE)

Charged DPG Wt. %	Mole per 10 kg of mixture	Sulfur decrease		Bound DPG (limiting values)	
		Reaction order, <i>n</i>	Rate constant, <i>k</i> · 10 ⁴	Mole %	Mole per 10 kg of mixture
0.5	0.24	ca. 1	1.04	100	0.24
1.0	0.48	ca. 0.9	2.69		
1.5	0.72	ca. 0.8	4.1		
2.0	0.95	0.75	4.9	53	0.50
3.0	1.43	0.7	6.1		
4.0	1.90	0.7	6.3	32	0.61
5.0	2.38	0.7	6.7		
6.0	2.85	0.7	6.2	31	0.88

with increasing initial base content, whereas, the absolute amount of diphenylguanidine which is bound in the vulcanizate, increases (column 6).

It is believed that the character of the relationships given in Figure 9 and Table IX would remain essentially the same if the initial sulfur concentration was varied.

In view of our present knowledge it must be assumed that the vulcanization with sulfur is a "clean" though somewhat complicated chemical reaction and the sulfur decrease with time during a sulfur cure actually measures the rate determining step. This is the ring opening of the S_8 rings to give open chains, a fact which was postulated and proved by Gordon¹⁶ and by others.

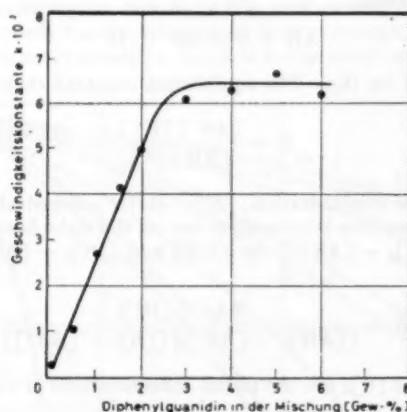


FIG. 9.—Rate constant of the sulfur decrease versus DPG concentration at 115° C (~1 mole of S_8 per 10 kg of mixture).

An explanation of the nature of Figure 9 shall follow. It should be noted at this point that sulfur dissolves in organic bases which contain little water and the solutions are red; their electrical conductivity is noticeable and the final conductivities are reached with a measurable rate. These phenomena probably are reactions of the bases with sulfur, which occur very rapidly at high temperatures.

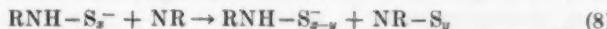
With reference to Krebs¹⁷ deliberations on the interaction of organic bases with sulfur, based on experiments in connection with the nature of the vulcanization, we would like to formulate the following reaction:



and



It is assumed that at high temperatures equilibrium is reached quickly and formation of $RNH-S_8^-$ anions is possible. These anions supply the vulcanization continuously with available sulfur. Therefore, the reaction with rubber may be formulated further



where NR = natural rubber.

Irrespective of whether Equilibrium (6) is reached rapidly and Reaction (8) proceeds considerably slower, or if one supposes that the two processes proceed with comparable rate, the base must be considered as a catalyst which becomes active through the formation of an intermediate compound. In this case, it is the negative ion on the right hand side of (6). For the calculation of the rate of sulfur decrease, however, it must be assumed that Equilibrium (6) is considerably faster than the rate of Reaction (8). It then becomes possible to determine the concentration of the intermediate compound by means of Equilibrium (6) and this value is used to calculate the rate of Reaction (8)¹⁸. The following calculation is obtained:

A general equilibrium



may be substituted for (6). The equilibrium constant then is

$$K = \frac{[AS^-][H^+]}{[AH][S]} \quad (10)$$

where $[AH]$ = base concentration; $[S]$ = sulfur concentration; $[AS^-]$ = concentration of the negative intermediate ion on the right hand side of (6). By substituting $[[AH]_0 - [AS^-]]$ for $[AH]$ and $[[S]_0 - [AS^-]]$ for $[S]$ (10) may be written:

$$K = \frac{[AS^-][H^+]}{[[AH]_0 - [AS^-]][[S]_0 - [AS^-]]} \quad (11)$$

whereby $[AH]_0$ and $[S]_0$ are the initial concentrations of the base and of the sulfur, respectively.

As a practical application to some of our experiments where the base concentration is greater than the sulfur concentration, one may write $[[AH]_0 - [AS^-]] \sim [AH]_0$ as an approximation, thus

$$K = \frac{[AS^-][H^+]}{[AH]_0 [[S]_0 - [AS^-]]} \quad (12)$$

and the concentration of the intermediate ion is

$$[AS^-] = \frac{K [AH]_0 [S]_0}{K [AH]_0 + [H^+]} \quad (13)$$

By considering Reaction (8), the change of the sulfur concentration with time is obtained

$$-d[S]/dt = k [AS^-] [NR] \quad (14)$$

Combining (13) and (14) furnishes for the rate of sulfur decrease

$$-d[S]/dt = \frac{k K [AH]_0 [S]_0 [NR]}{K [AH]_0 + [H^+]} \quad (15)$$

The result of Equation (15) would not be changed if it were assumed that the reaction product on the right hand side of (6) is practically nondissociated

or if amine and sulfur in the sense of Krebs come to an equilibrium with an amine polysulfide $\text{RH}_2\text{N}^+ \rightarrow \text{S}-\cdots-\text{S}^-$ of betaine-like structure. The result of such an assumption would be $[\text{H}^+] = 1$ and therefore

$$-d[\text{S}]/dt = \frac{k K [\text{AH}]_0 [\text{S}]_0 [\text{NR}]}{K [\text{AH}]_0 + 1} \quad (16)$$

As long as the concentration of the catalyst AH (in our case the base) is small, so that $K [\text{AH}]_0$ is small compared with $[\text{H}^+] = 1$, the rate of sulfur decrease increases linearly with the base concentration. If, however, with growing base concentration the $K [\text{AH}]_0$ part of the denominator of (15) approaches or exceeds the second part of the denominator, the rate of sulfur decrease finally becomes constant; i.e., it is independent of the base concentra-

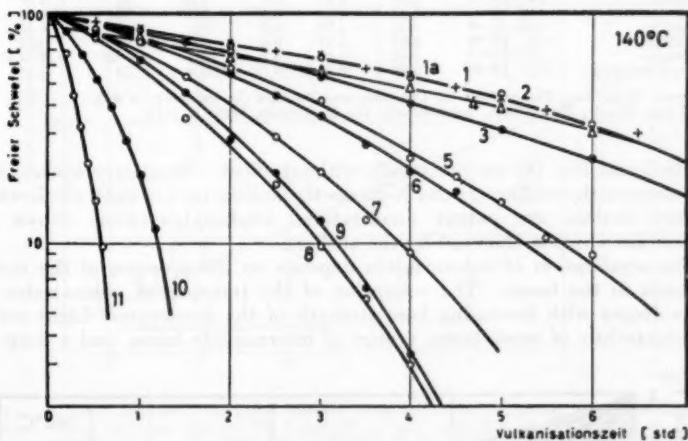


FIG. 10.—Decrease of the sulfur concentration during the reaction with NR in presence of equimolar additions of various organic bases at 140° C. For meaning of plot points see Figure 12.

tion. It is readily apparent that the relationships in Figure 9 are well defined by the Equations (15) and (16). For this reason we believe it is justified to interpret the reaction of sulfur with natural rubber in presence of bases as an intermediate catalysis. Furthermore, the discussion remains the same, when the rate $-d[\text{S}]/dt$ is substituted for the rate constant (ordinate in Figure 9).

The reaction of NR with sulfur in presence of various organic bases at 140° C.—It appears that the kinetics of the diphenylguanidine accelerated sulfur cure has certain similarities with enzyme reactions. Since it has been frequently said that a connection exists between accelerating action and base strength¹⁹, a series of bases were investigated (140°, one mole of base and one mole of sulfur per 10 kg of mixture). From Figure 10 it appears that none of the bases accelerate the sulfur decrease in such a manner as to create a first order reaction. The reaction order again was found to be in the range of 0.5 to 0.7 (compare Table XI, column 5). Confirmation of the experimentally determined reaction order is given by the straight line curves in Figure 11.

Discussion of Figure 11: Tertiary bases such as dimethylaniline (Curve 1)

TABLE XI

RELATIONSHIPS BETWEEN RATE CONSTANT OF THE SULFUR DECREASE AND BASE STRENGTH DURING THE VULCANIZATION OF NATURAL RUBBER IN PRESENCE OF VARIOUS ORGANIC BASES AT 140° C (1 MOLE OF BASE AND 1 MOLE OF S₈ PER 10 KG OF MIXTURE)

Base	K_B	Dissociation constant (25° C) —log K_B (pK)	Sulfur decrease		$\frac{c_B}{c_0} \cdot 100$ (mole %)	Bound base (limiting values) Mole of base per 10 kg of mixture
			Reaction order, n	Rate constant, $k \cdot 10^3$		
Sulfur only	—	—	—	0.6	2.30	—
N-Dimethylaniline	$11.5 \cdot 10^{-10}$	8.94	5.16	0.2	2.02	3 0.03
N-Diethylaniline	$3.65 \cdot 10^{-10}$	7.44	6.66	0.3	2.13	0 0.0
Monomethylaniline	$5 \cdot 10^{-10}$	9.30	4.80	0.7	3.09	4-17 0.04-0.17
Monooethylaniline	$12.9 \cdot 10^{-10}$	8.89	5.21	0.7	2.43	3 0.03
α-Naphthylamine	$0.84 \cdot 10^{-10}$	10.08	4.02	0.5	4.00	43 0.43
o-Toluidine	$2.47 \cdot 10^{-10}$	9.61	4.49	0.7	4.87	21 0.21
Aniline	$3.82 \cdot 10^{-10}$	9.42	4.68	0.5	5.96	38 0.38
m-Toluidine	$4.92 \cdot 10^{-10}$	9.31	4.79	0.5	7.9	17 0.17
p-Toluidine	$11.8 \cdot 10^{-10}$	8.93	5.17	0.6	7.9	22 0.22
Benzylamine	$2.35 \cdot 10^{-5}$ *	4.63	9.47	0.7	22.2	27-62 0.27-0.47
Diphenylguanidine	$13.0 \cdot 10^{-9**}$	3.89	10.21	0.75	53.9	54 0.54

* From: D'Ans-Lax, Taschenbuch für Chemiker und Physiker (Berlin, 1943), p. 845.

** From: Staude, Phys.-Chem. Taschenbuch, Vol. II (Leipzig, 1949), p. 1616.

and diethylaniline (2) are practically without effect. Secondary amines such as N-monomethylaniline (3) and N-monoethylaniline (4) are weak accelerators. Primary amines are potent accelerators. Diphenylguanidine shows the greatest acceleration observed by the authors.

The acceleration of vulcanization depends on the presence of the mobile hydrogen in the bases. The coloration of the transparent vulcanizates becomes deeper with increasing base strength of the accelerator: Light yellow is characteristic of weak bases, orange of intermediate bases, and a deep red

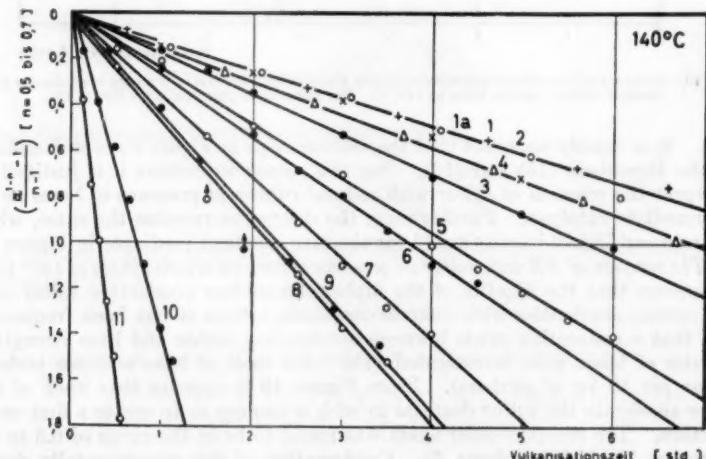


FIG. 11.—Decrease of the sulfur concentration according to a reaction order, $n = 0.5$ to 0.7, during the reaction with NR at 140° C in presence of equimolar additions of various organic bases. For meaning of plot points see Figure 12.

color is produced by strong bases. These are the same colorations which occur when sulfur is dissolved in organic bases. After adding a little water the conductivity increases with increase in coloration.

The fraction of the chemically bound base generally increases with increasing accelerating action. Nonaccelerating bases can be recovered quantitatively (Table XI, columns 7 and 8).

Since all the experiments were run with the same initial sulfur concentration and with equimolar amounts of bases, the rate constants of the sulfur decrease can be compared with one another. It was then possible to investigate whether a connection existed between the rate constants and the base strengths.

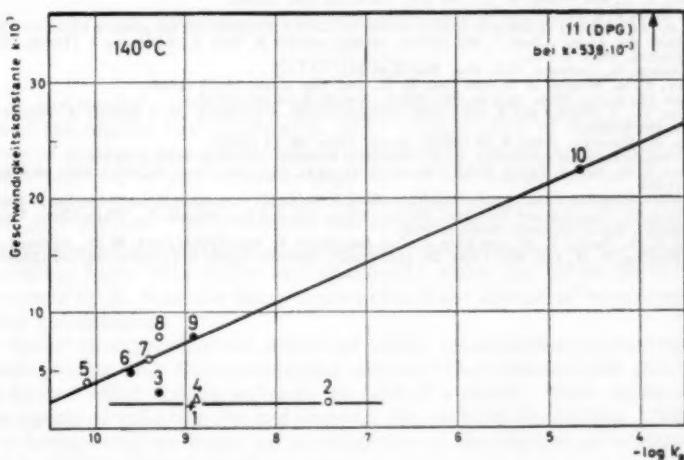


FIG. 12.—Rate constant of the sulfur decrease versus the negative logarithm of the base dissociation constants during the vulcanization of NR (1 mole of base and 1 mole of S₈ per 10 kg of mixture, vulcanization temperature 140° C.). The plot points for Figures 10, 11 and 12 have the meaning indicated in the following table. nur Schwefel means only sulfur.

- | | |
|-------------------------------|-------------------------------|
| 1a. Only sulfur (X) | 6. o-Toluidine (●) |
| 1. N-Dimethylaniline (+) | 7. Anilin (○) |
| 2. N-Diethylaniline (○) | 8. m-Toluidine (○) |
| 3. N-Monomethylaniline (●) | 9. p-Toluidine (●) |
| 4. N-Monoethylaniline (Δ) | 10. Benzylamin (●) |
| 5. α -Naphthylamin (○) | 11. N-N'-Diphenylguanidin (○) |

If the rate constants of Table XI are plotted versus the negative logarithm of the dissociation constant K_B^{20} , Figure 12 is obtained. A linear relationship exists between these constants for α -naphthylamine (Curve 5), o-toluidine (6), aniline (7), m-toluidine (8), p-toluidine (9) and benzylamine (10). All of these compounds are primary amines. Such a relationship does not exist for the tertiary amines dimethylaniline (1) and diethylaniline (2) and for the secondary amines N-monomethylaniline (3) and N-monoethylaniline (4). Since DPG drops entirely out of this scale it is concluded that the relationships as represented in Figure 12 are only valid for constitutionally comparable amines. These results confirm those of Kratz and others²¹.

A paper on the determination of sulfur and of bases in extracts of vulcanizates is in preparation and related investigations are in progress.

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THE VULCANIZATION OF ELASTOMERS. 16. THE VULCANIZATION OF NATURAL RUBBER WITH SULFUR IN THE PRESENCE OF DITHIOCARBAMATES (I) *

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INTRODUCTION

In the results¹ published in the last communication of this series, we discussed the organic base-accelerated sulfur vulcanization of natural rubber as a case of catalysis by an intermediate component. In the further discussion of such a concept, a more accurate inspection of the dependence of the rate of sulfur decrease on the concentration of the diphenylguanidine accelerator is of particular interest. This becomes plausible when one tries to combine the forthcoming kinetic relations with the newer interpretation of the interaction of organic bases with sulfur and specifically when one draws on the ideas developed by H. Krebs on the interpretation of the kinetics of base-accelerated sulfur vulcanization.

Krebs² in expressing the nature of sulfur vulcanization accelerated with xanthogenates and dithiocarbamates assumed that intermediate compounds are formed which contain sulfur in the form of a chain³. Such chains are the true agents of vulcanization and transmit the sulfur to the rubber. With this as a background we began an investigation of the kinetics of vulcanization with a dithiocarbamate as the accelerator.

This type of vulcanization has already been subjected to study⁴ with the conventional physical properties of the vulcanizates usually being drawn on as criteria for the observed phenomena. The kinetics of the process have been investigated¹⁰ less frequently.

One must distinguish between the ammonium dithiocarbamate type and the dithiocarbamates of heavy metals⁵. The first is ionic in nature and as such is sensitive to oxygen and moisture in the air and has, as well, little stability at higher temperatures. The latter, that is, the dithiocarbamates of zinc, copper, and cobalt, are internal-complex compounds. They are distinguished by their good solubility in organic solvents such as acetone, ethyl acetate, dioxan, tetrahydrofuran, and others.

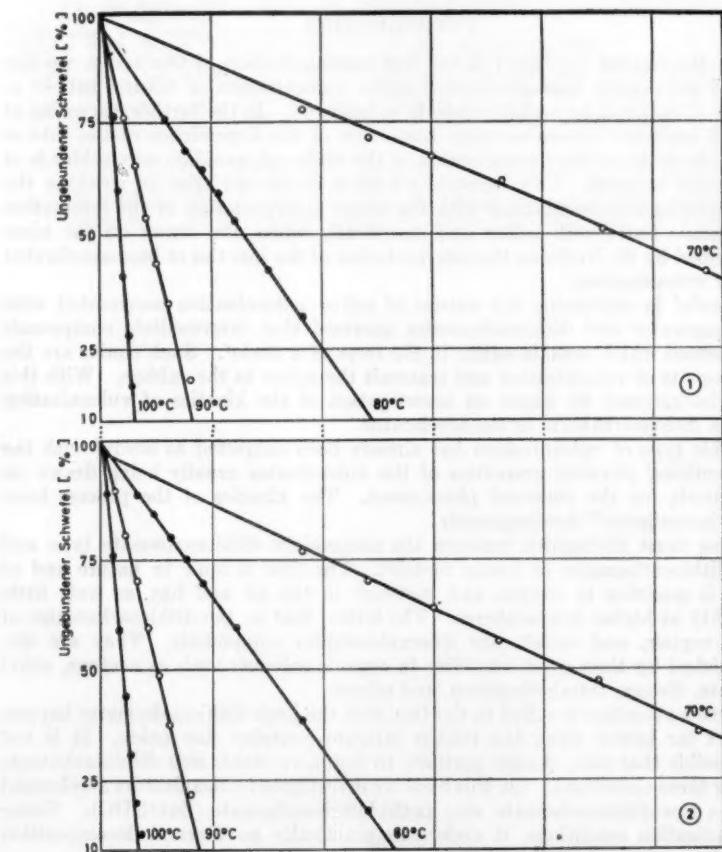
One's attention is called to the fact that the ionic dithiocarbamates happen to act far better when the rubber mixture contains zinc oxide. It is not impossible that they change partially to the more stable zinc dithiocarbamate under these conditions. On this basis we investigated vulcanization accelerated with a zinc dithiocarbamate, zinc diethyldithiocarbamate (ZnDED). Under vulcanization conditions, it undergoes practically no thermal decomposition and does not react with rubber.

* Translated by Seward and Mary Averill for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi* Vol. 10, WT 214 to 222, September 1957. In order to save space six tables from the original have been omitted from this translation.

RESULTS AND DISCUSSION

We investigated the vulcanization of natural rubber with sulfur (2.565 g per 100 g of stock) in the presence of ZnDEDC at 70°, 80°, 90°, and 100° C and varied the molar ratios of sulfur and ZnDEDC in the mixture within wide limits. The decrease in concentration of sulfur and dithiocarbamate with vulcanization time, t , was measured, as well as the increase of crosslinking expressed by the reciprocal swelling index in benzene, $1/Q_t$ (grams of swelling agent per gram of vulcanizate).

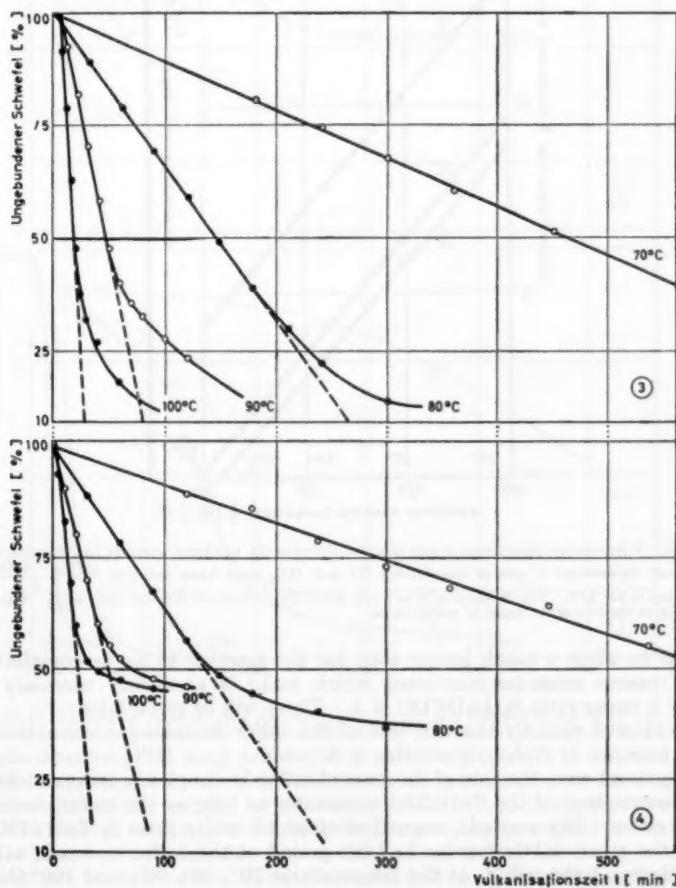
The results are compiled in the *Kautschuk und Gummi* text as Tables I through IV and are not shown in the present version. They include sulfur and ZnDEDC content in the final product found for each single reaction time and temperature in per cent of starting amount, the reciprocal swelling



FIGS. 1 to 4.—Decrease of sulfur concentration during vulcanization of natural rubber in the presence of various amounts of ZnDEDC per 100 g of stock. The abscissa is free sulfur in per cent of the sulfur compounded and the ordinate is cure time in minutes. The sulfur compounded was 2.565 g per 100 g of stock in each case. The stocks for Figures 1 to 4 contained, respectively, 7.240, 3.620, 1.810, and 0.905 g of ZnDEDC per 100 g of stock.

index, $1/Q_t$, and in three cases (Tables I, II, and III) also the difference $(1/Q_\infty - 1/Q_t)$. Figures 1 through 4 show the decrease of sulfur with reaction time using the molar proportions $S_8:ZnDEDCC$ as 1:2, 1:1, 1:0.5, and 1:0.25. The per cent of uncombined sulfur is plotted against the cure time in minutes.

While it has been shown that the decrease of sulfur during vulcanization in the presence of mercaptobenzothiazole and zinc oxide, or zinc benzothiazolyl mercaptide, is first order⁶, and in the presence of an organic base is fractional order⁷, and finally that the reaction of sulfur with rubber in the presence of zinc oxide is always first order⁷, it is now shown that the concentration of sulfur, when the vulcanization is accelerated with ZnDEDCC, decreases according to zero order kinetics⁸. To be sure, the slope of the sulfur concentration over practically the whole range of reaction is linear only when the molar ratio $S_8:ZnDEDCC$ is at most equal to 1. But even then in the range of low reaction



Figs. 1 to 4.—Continued.

extents deviations occur in the direction of higher reaction orders and the greater the molar ratio S_8 :ZnDEDC, the sooner these are noticeable.

In comparison to other curing systems, vulcanization accelerated with dithiocarbamates is an extraordinarily rapid process for which the analytical range lies between about 70° and 100° C as shown in Figures 1 through 4. But to make the most of the catalytic activity of the dithiocarbamate, it is well to prepare the compounds so that they contain at least one mole of dithiocarbamate to one mole of S_8 . Otherwise, one has to expect after a very rapid initial reaction, an intrinsically slow decrease in sulfur, and correspondingly

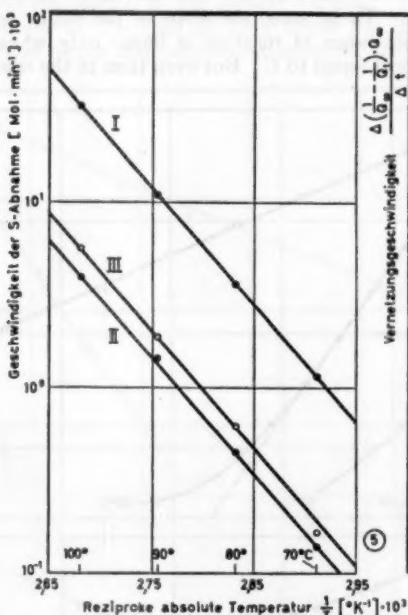
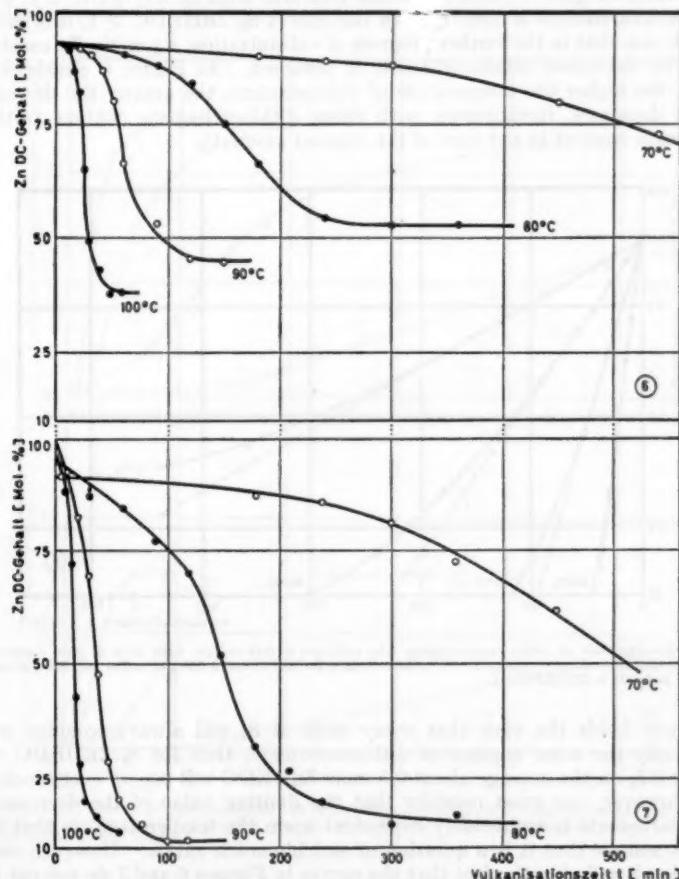


FIG. 5.—Temperature dependence of rate of sulfur decrease (I), left hand ordinate, in 10^3 moles/min; temperature dependence of rate of crosslinking (II and III), right hand ordinate, $\frac{(1/Q_m - 1/Q_i)Q_m}{\Delta t}$. The abscissa is $10^3 \cdot 1/T$. For II, moles of S_8 to moles ZnDEDC = 1 and, for III, this ratio = 0.5. The rate data apply to the zero order region of curing rates.

one has to allow a much longer time for the reaction to go to completion. Other reasons must be mentioned which make it absolutely necessary to employ a molar ratio S_8 :ZnDEDC = 1. These will be given later.

We showed recently that the rate of the sulfur decrease for vulcanization in the presence of diphenylguanidine is dependent upon DPG concentration⁷. In the present case, the rate of decrease of sulfur is completely independent of the concentration of the ZnDEDC accelerator as long as the sulfur decrease is zero order. For example, regardless of which molar ratio S_8 :ZnDEDC is given, the mean values for the half-life period of the sulfur decrease, taken from Figures 1 through 4, at the temperatures 70°, 80°, 90°, and 100° C are 460, 140, 50, and 20 minutes.

If one plots logarithmically the mean values of the rate against $1/T$, as shown in Figure 5, one obtains Line I. From its slope may be computed an activation energy of 29.2 kcal, a value in excellent agreement with the activation energies found for the decrease in sulfur for vulcanizations in the presence of diphenylguanidine (29.8 kcal) or mercaptobenzothiazole (30.5 kcal)⁹.



FIGS. 6 and 7.—Decrease of mole per cent (ordinate) of ZnDEDC as a function of cure time (minutes). Figure 6 is for a ratio 1 mole of S₈ to 1 mole of ZnDEDC and Figure 7 is for a ratio twice as great.

In dithiocarbamate accelerated vulcanization a certain amount—and under certain conditions, all—of the accelerator is used up; i.e., is not recoverable. In Figures 6 and 7 we show the decrease of dithiocarbamate content in relation to vulcanization time, e.g., for two molar ratios, S₈:ZnDEDC = 1 and 2. One observes in each case a relatively rapid falling off in dithiocarbamate content—the higher the temperature, the more precipitous is the falling off.

If the molar ratio $S_8:ZnDEDC = 2$, practically all the zinc dithiocarbamate is finally used up, and that is also the case when $S_8:ZnDEDC = 4$ (not shown here). But when the dithiocarbamate content increases, i.e., when the molar ratio $S_8:ZnDEDC$ becomes smaller, all of the dithiocarbamate is not finally used up. When $S_8:ZnDEDC = 1$, a considerable portion of the accelerator is recoverable (Figure 6); and in rubber mixtures with $S_8:ZnDEDC < 1$, even less dithiocarbamate is used up. In the case of $S_8:ZnDEDC \leq 1$, it is shown in each case that in the further progress of vulcanization, a practically constant value for decreased dithiocarbamate is obtained. As Figure 6 clearly illustrates, the higher the temperature of vulcanization, the greater the decrease; and it decreases, furthermore, with rising dithiocarbamate content (dithiocarbamate content in per cent of the original amount).

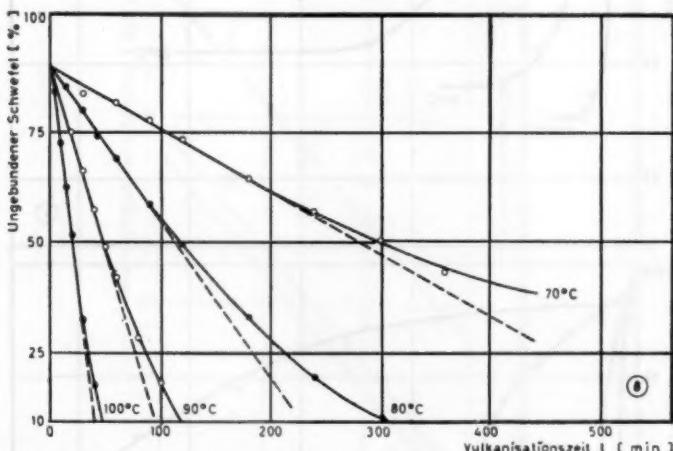


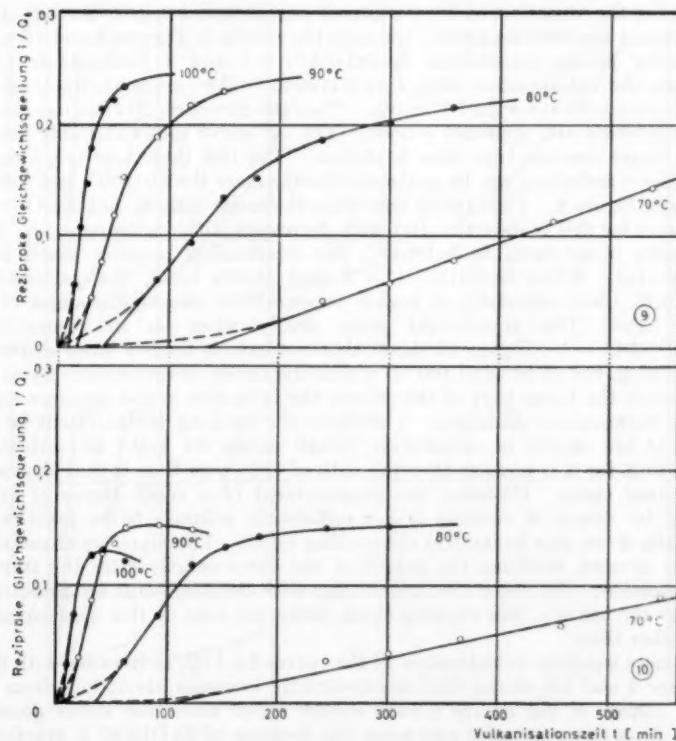
Fig. 8.—Decrease of sulfur concentration (the ordinate is free sulfur) with time of cure (minutes). The stock (natural rubber) contained 4.075 g ZnO, 3.620 g ZnDEDC and 2.565 g of sulfur per 100 g of stock. Ratio of moles S_8 to ZnDEDC = 1.

If one holds the view that every mole of S_8 will always combine with practically the same amount of dithiocarbamate, then for $S_8:ZnDEDC = 1$ and/or 0.5, on the average about 0.5 mole ZnDEDC will use up every mole of S_8 . However, one must consider that the limiting value of the decrease of dithiocarbamate is appreciably dependent upon the temperature, so that one cannot assume that it is a question of stoichiometric ratios. However, one's attention is called to the fact that the curves in Figures 6 and 7 do not cut the ordinate at 100 per cent when $t = 0$, from which one must conclude that the reaction sets in immediately upon the mixing of the dithiocarbamate, but without the vulcanization taking place directly, since the curves in Figure 1 through 4 show no sign of prevulcanization.

By comparison of Figure 3 and Figure 7, it is shown that the sulfur decrease always begins to deviate from the course of zero order when the decrease in concentration of zinc dithiocarbamate slows down significantly or the limiting value of dithiocarbamate is about reached. Thereafter a correlation exists between the variation of the time dependent sulfur concentration and the

dithiocarbamate content. However, the latter shows an entirely different kinetic form than the sulfur decrease. This needs no particular explanation.

In this connection, it is not without interest that stocks which contain ZnO besides sulfur and zinc dithiocarbamate behave somewhat differently. The results, found for a ratio of $S_2/ZnDEDC = 1$, are given in Table VI of the original article and omitted in this translation. The variations of the concentration of sulfur with time at similar temperatures as in Figures 1 through



Figs. 9 and 10.—Cure time dependence of reciprocal equilibrium swell, $1/Q_e$, at various temperatures for mixtures containing 2.565 g of sulfur per 100 g of stock. For Figure 9 moles S_2 to moles ZnDEDC = 1 and for Figure 10 this ratio = 4.

4 are shown in Figure 8 and this is again of zero order with its deviation in the range of less reaction. One observes also—as far as is detected from a single series of experiments—approximately the same half-life as in the corresponding vulcanizations in the absence of ZnO; but it now becomes evident that immediately upon mixing, a definite amount of sulfur enters into the reaction; for the curves in Figure 8 do not cut the ordinate at 100 per cent when $t = 0$ which they always do in studies in the absence of ZnO. The decrease of dithiocarbamate content under these conditions is remarkably less than in the experiments in the absence of ZnO and plainly reaches its limit

directly after the setting in of vulcanization, as shown clearly in the analytical data in Table VI. But it also shows that the higher the temperature, the more dithiocarbamate is used up. One sees that in vulcanization with sulfur and zinc dithiocarbamate, the ZnO itself plays a role even if the rate of decrease of sulfur does not appear to be influenced appreciably.

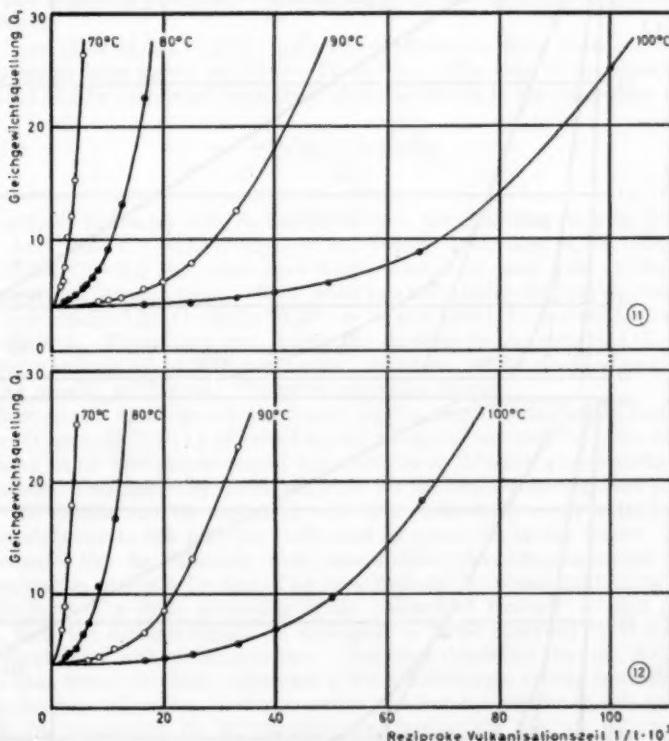
Vulcanizates prepared with zinc dithiocarbamate as accelerators are excellent. Therefore, it is of interest to investigate the true crosslinking reaction. This can be done by the measurement of the reciprocal equilibrium.

As for the variation of the reciprocal equilibrium swell, $1/Q_t$, with time (benzene as the swelling agent), we show the results in Figures 9 and 10 using the molar mixing proportions $S_8:\text{ZnDEDCC} = 1$ and 4 (ordinate is $1/Q_t$; abscissa, the vulcanization time, t , in minutes). The curves are linear at the outset, especially so for the 70° curve. Then the curves rapidly become convex to the ordinate and approach a limit. The 70° curve shows this only after a much longer reaction time than is plotted. The fact that there is a limiting value for crosslinking can be gathered directly from the 80° , 90° , and 100°C curves in Figure 9. The same is true when the molar ratio $S_8:\text{ZnDEDCC} = 0.5$ (no curve for this is shown). But with decreasing dithiocarbamate, i.e., with increasing molar ratio $S_8:\text{ZnDEDCC}$, the relationship becomes much more complicated. When $S_8:\text{ZnDEDCC} = 2$ (not shown here), the variation of $1/Q_t$ with time, especially at higher temperatures, displays changes of its curve habit. This stands out more clearly when—as in Figure 10— $S_8:\text{ZnDEDCC} = 4$. Figure 10 shows that not only is there a lesser degree of crosslinking, but at 90° and 100°C a clear indication of reversion. By extrapolation of the linear part of the curves, the induction period becomes larger as the temperature decreases. Therefore, the swelling measurement in the range of low degree of crosslinking (small values for $1/Q_t$) is particularly interesting, for it is possible that the path of $1/Q_t$ with time is that shown by the dotted curve. However, the measurement of a small degree of crosslinking by means of swelling is not sufficiently accurate to be practicable, especially if one uses benzene as the swelling agent. Therefore, we abandoned, for the present, studying the details of the curve shortly after the start of vulcanization. We are of the opinion that such measurements are practicable only by the use of a poor swelling agent, so we will take up this question anew at another time.

A more exacting consideration of the curves for $1/Q_t$ as it varies with time (Figures 9 and 10) shows that as crosslinking increases, deviations from the linear course of the curves always occurs about when the sulfur decrease varies from the zero order and when the decrease of ZnDEDCC is practically complete. From that, one must conclude that the decrease in sulfur and the crosslinking in these vulcanization reactions are interdependent processes.

Summing up, we have the following phenomena: In the vulcanization of natural rubber with sulfur in the presence of a zinc dithiocarbamate, crosslinking is of zero order over a fixed range of reaction with an increasing induction period with a decrease in temperature (different from the kinetics of sulfur decrease), or with an initially retarded course. The crosslinkage varies, like the sulfur decrease, according to zero order kinetics; and when the molar ratio $S_8:\text{ZnDEDCC} = 1$ is exceeded, i.e., when the content of sulfur is kept constant and the dithiocarbamate added is successively decreased, the degree of crosslinkage finally decreases markedly and a reversion of the crosslinking reaction is superimposed at higher vulcanization temperatures [maxima in the curves $1/Q_t = f(t)$].

In our opinion, from the above, it would be expedient for the compounder for a vulcanization accelerated with ZnDEDC to mix sulfur and ZnDEDC in a molar ratio S_8 :ZnDEDC at most 1. When, for example, the rubber compound contains less ZnDEDC than corresponds to the molar ratio indicated (S_8 :ZnDEDC > 1), one must conclude according to existing results that no optimum degree of crosslinkage can be reached and at higher vulcanization temperatures a reversion (in crosslinkage) will result. This will without

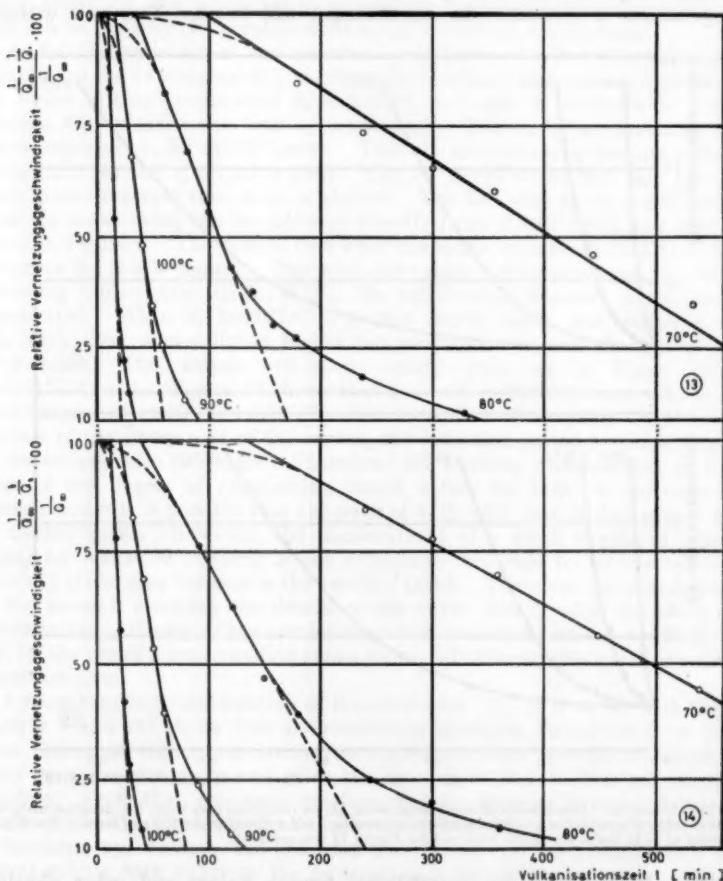


Figs. 11 and 12.—Dependence of equilibrium swell, Q_e , on reciprocal cure time, $1/t$, demonstrating the limiting value of equilibrium swell for mixtures containing 2.565 g of sulfur per 100 g of stock. For Figure 11 moles of S_8 to moles ZnDEDC = 0.5 and for Figure 12 this ratio = 1.

question be indicated by conventional tension values and other physical properties (possibly aging stability). Finally it will be scarcely possible with a rubber mixture of such composition to obtain vulcanizates which have reproducible physical properties. If one does not take these things into consideration, then the sulfur combines rapidly only in the initial stages of the vulcanization and the less ZnDEDC that is present, the sooner the decrease in concentration of sulfur is retarded and the more it is retarded, as has been mentioned before. Making the most of the "ultra-accelerator" provided by the presence of ZnDEDC on the one hand, and providing vulcanizates with optimum physical properties on the other, are combined by the right selection

of the molar ratio of S_8 :ZnDEDC which the present research results set at about equal to 1.

In view of the results met with in the kinetics of the crosslinking reaction, it is not recommended to assign equivalent value to all the swelling measurements in arriving at the actual values for the rate of crosslinking. Conse-



Figs. 13 and 14.—Cure time dependence of relative crosslinking rate for mixtures containing 2.565 g sulfur per 100 g of stock. For Figure 13 moles of S_8 to moles of ZnDEDC = 0.5 and for Figure 14 this ratio = 1.

quently, we limited ourselves to measurements obtained for vulcanizates with the molar ratio S_8 :ZnDEDC = 1 and 0.5, referred to in Tables I and II (columns 5 and 6), because they were most nearly suitable for such calculations.

Next we show with Figures 11 and 12 the graphic determination of the limiting values for the swelling index by plotting Q_e against the reciprocal of cure time. One sees that the curves in both cases converge at smaller values

of $1/t$ and can be extrapolated to intersection at the ordinate. It is shown that the limiting values of the swelling index agree at the molar ratios $S_8:\text{ZnDED}\text{C} = 1$ and 0.5. That may also be expected when the same cross-linkage mechanism terminates when the sulfur concentration becomes constant. If one considers that the swelling values of the vulcanizates will also be dependent upon the extent of mastication of the mixtures, there arises a clear-cut method of carrying out vulcanization research; for in the present investigation one realizes a practically constant degree of decomposition of the starting materials.

If one plots $(1/Q_\infty - 1/Q_t) / Q_\infty \cdot 100$ against cure time, then one obtains the straight lines shown in Figures 13 and 14. The rate of the crosslinking reaction can be calculated from their slopes as shown in the expression

$$\frac{\Delta(1/Q_\infty - 1/Q_t)Q_\infty}{\Delta t}$$

One obtains for molar ratio $S_8:\text{ZnDED}\text{C} = 1$, the following rates at 70° , 80° , 90° , and 100° C , respectively, 0.135, 0.450, 1.45, and 4.00, while for $S_8:\text{ZnDED}\text{C} = 0.5$ the rates were 0.160, 0.66, 1.93, and 5.80 at the same temperatures, respectively. If one plots logarithmically the rate against $1/T$, then one obtains Line II ($S_8:\text{ZnDED}\text{C} = 1$), and Line III ($S_8:\text{ZnDED}\text{C} = 0.5$) in Figure 5. These lines run practically parallel to the plot of $1/T$ versus [moles/minute] $\cdot 10^3$ of sulfur decrease; therefore, sulfur decrease and cross-linking possess, in this case, the same activation energy.

Because we investigated kinetically only a single initial concentration of sulfur (1 mole S_8 in 10 kg of mixed stock) we cannot say that for other concentrations, other viewpoints should not result in a different quantitative interpretation. One naturally questions, even for the single concentration studied, how the results can be explained. In this connection, every consideration raises obstacles to the problem that must be overcome in the future. Thus, we should like to establish that zinc dithiocarbamate-accelerated sulfur vulcanization proceeds by way of an intermediate compound containing sulfur in the form of a chain according to the concept of Krebs¹⁰. If this proved true, then the kinetics should be analogous to those observed for vulcanization accelerated with an organic base. But since this is not the case, it appears to us that one of the basic questions is the circumstance arising from the zero order decrease of sulfur. Let us consider whether the answer to this question could be reconciled by a vulcanization mechanism via an intermediate compound.

If one assumes, for example, that the accelerator ZnDED C is completely insoluble in the rubber (though this might not be quite correct) at the higher temperatures at which the reaction proceeds with greater and more measurable velocity, then one can advance the theory that the intermediate compound would saturate the surface of crystalline dithiocarbamate. It is understandable that the sulfur under these conditions will "react away" according to zero order kinetics. But it is not understandable why the rate of decrease of sulfur does not respond to the amount of ZnDED C used and so increase when an increasing amount of ZnDED C is used. Clearly an increase in ZnDED C added to the compound would amount to an enlargement of surface and therefore result in an increase in the concentration of the intermediate compound. Finally, one must question why sulfur itself remains unused in the vulcanizate

in the case of higher amounts of dithiocarbamate, and does not react in a zero order fashion right up to the end of the reaction. One can reasonably suppose—analogously to thiuram disulfide decrease as well as to dithiocarbamate increase in thiuram disulfide vulcanization¹¹—that diffusion effects are the cause of the observed deviation from zero order kinetics. One can then propose that the surface of dithiocarbamate crystals in such a case is blocked by a yet unknown compound involving spent dithiocarbamate, i.e., the access of sulfur to unreacted dithiocarbamate is blocked. These ideas may be tested for validity.

More obvious, possibly, is the assumption that an intermediate compound formed from ZnDEDC and sulfur may be soluble to a limited degree in rubber at the temperature of vulcanization so that its reaction with rubber takes place in a saturated solution. But it is not fully understood why the decrease in sulfur does not remain zero order over the entire range of vulcanization as long as sufficient amounts of dithiocarbamate are present. The intermediate compound must go into solution as it disappears in further reaction. After all, rate of sulfur decrease, independent of dithiocarbamate content, can be better reconciled by the assumption of transport of reaction by way of a saturated solution.

It is clear that it is still difficult from the present results to derive detailed definite conclusions with respect to all aspects. Therefore, it will be necessary not only to investigate kinetic effects of the initial concentration of sulfur, but also to study approaches other than kinetic¹². It seems to us one may seek an explanation of zero order sulfur decrease possibly in the solubility results of zinc dithiocarbamate as well as through some unknown intermediate compound. Our knowledge of the solubility of most vulcanization agents and accelerators as well as of many other important rubber additives is indeed incomplete. Therefore, much experimental work must still be done before one may see clearly those things which are so important to the kinetics of vulcanization.

ANALYTICAL PROCEDURES

The procedure used for the determination of free sulfur in the vulcanizate-extracts was similar in principle to the method proposed by Scheele and Ilischner-Gensch¹³ (conversion of sulfur to thiocyanate by means of KCN followed by the conductometric titration of SCN⁻ with AgNO₃). It was modified as follows:

One to two gram sample of pulverized vulcanizate was extracted with a benzene-alcohol mixture (1:1) at room temperature in the dark for four to five days with repeated change of the exhausted extraction agent. The combined portions of the extract, which contain besides uncombined sulfur the zinc dithiocarbamate present, were treated with an excess of a 5 per cent water solution of KCN for 2-3 hours at 60° C. (One can just as well leave the reaction mixture 4-5 days in the dark at room temperature since the formation of thiocyanate proceeds quantitatively under these conditions.) The excess KCN as well as that of zinc dithiocarbamate interfering with the titration with AgNO₃ is destroyed by the addition of 0.2-0.5 ml formic acid (according to the amount of zinc dithiocarbamate present) and evaporated to dryness on a water bath under reduced pressure. The residue was dissolved with distilled water with the aid of some alcohol and made up to 100 ml. An accurately measured portion of this solution is then titrated conductometrically with silver nitrate.

For the determination of zinc dithiocarbamate the vulcanizate is extracted with reagent grade acetone (distilled over CaO). The combined extracts, after previous concentration to a smaller volume, are diluted to a definite volume. An aliquot of this solution is titrated conductometrically according to the method of Scheele and Gensch¹⁴ with from 0.02 to 0.05 N hydrochloric acid.

For measuring swelling, rectangular slices of vulcanizate of about 1 gram are placed in a closed weighing vessel with benzene and allowed to swell for 48 hours at 25° C. The benzene having been absorbed, the swollen vulcanizate is quickly blotted free of adhering benzene with hard filter paper. The sample is transferred to a tared weighing bottle, carefully stoppered, and weighed immediately. The open weighing bottle containing the swollen material is then placed in an 80° C drying oven for 16 hours. In this way the vulcanizate loses the swelling agent. The sample is cooled in a desiccator and weighed. Subtraction of the weight of the empty weighing vessel from the result of the first weighing gives the weight of swollen rubber, and from the result of the second weighing gives the dry weight of gel. By difference in weight of swollen and dried vulcanizate, one obtains the amount of swelling agent absorbed in grams. The amount of swelling agent is expressed per gram of vulcanizate and in the text is designated Q_t . The reciprocal, $1/Q_t$, is a measure of the degree of crosslinking.

SUMMARY

The kinetics of vulcanization of natural rubber with sulfur (initial concentration: 1 mole S₈ in 10 kilograms of mixture) was investigated in the presence of varying amounts of zinc diethyldithiocarbamate (ZnDED^C). The following results were obtained.

1. At all temperatures and, depending upon the dithiocarbamate content of the mixture, over practically the entire, or at least the greater, extent of vulcanization, sulfur decrease is a zero order process.
2. The rate of sulfur decrease is, as long as it proceeds according to zero order, independent of the molar ratio S₈:ZnDED^C. From the slope of the log rate versus 1/T plot is derived an activation energy of 29.2 kcal.
3. During vulcanization the dithiocarbamate content declines as long as the sulfur decrease follows the zero order. With decreasing starting content of dithiocarbamate, the stock finally uses up all the zinc dithiocarbamate during vulcanization. In other cases, a constant limiting value of dithiocarbamate decrease appears.
4. When zinc dithiocarbamate and zinc oxide are both present, sulfur decrease again takes place according to zero order. Under these conditions the process will use up less dithiocarbamate and shortly after the onset of vulcanization a constant final value of dithiocarbamate appears.
5. After the initial lag, crosslinking, measured by reciprocal equilibrium swell in benzene, proceeds according to zero order over the major extent of vulcanization. The temperature function of relative rates of crosslinking furnishes an activation energy similar to that for the rate of sulfur decrease.
6. Reciprocal equilibrium swell deviates from zero order time dependence as soon as the dithiocarbamate decrease reaches its final value, and the sulfur decrease also experiences a considerable lag.
7. It is shown that the limiting value of equilibrium swell increases as the starting content of dithiocarbamate decreases and also that reversion sets in

at higher temperatures. When the molar ratio of mixing S₈:ZnDEDC amounts to 1 or to 0.5, the limiting value of the swelling index is reached independent of temperature, i.e., the degrees of crosslinking are the same for these two ratios.

The investigations will be continued.

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- ¹ Compare Scheele, W., and Cherubim, M., *Kautschuk u. Gummi* **10**, 185 (1957).
- ² Krebs, H., *Gummi u. Asbest* **8**, 68 (1953) as well as *Angew. Chem.* **65**, 293 (1955).
- ³ Of course, according to Krebs even more evident indications of a reaction between zinc dithiocarbamate and sulfur appear in pyridine solution. Krebs supposes that the reaction is facilitated by a base approaching the coordinated zinc while it opens the four-membered ring of the complex. He could not isolate the compounds formed.
- ⁴ Compare, e.g., Twiss, D. F., Brasier, S. A., and Thomas, F., Lecture given at the University of Birmingham, January 26, 1922 [*J. Soc. Chem. Ind.* **41**, 81 (1922)]. In this discourse are found additional literature references. A work which furnishes a certain insight into the kinetic relations of vulcanization accelerated with dithiocarbamate was conducted by Zapp, R., and others, *J. Polymer Sci.* **6**, 331 (1950). The experiments started with butyl rubber and employed as accelerator the dithiocarbamate of tetravalent tellurium.
- Compare also, Farmer, E. H., "Advances in Colloid Science", Vol. II, Rubber, New York, 1946, p. 332 ff.
- ⁵ A very exhaustive summary of experimental results from the analysis of dithiocarbamate has been given by Gleu, K., and Schwab, R., *Angew. Chem.* **62**, 320 (1950).
- ⁶ Lorenz, O., and Echte, E., *Kautschuk u. Gummi* **10**, 23, 81 (1937).
- ⁷ Compare Scheele, W., and Cherubim, M., loc. cit.¹
- ⁸ We come to the result similar to that of van Alphen, J., *Angew. Chem.* **66**, 197 (1954), in which vulcanization accelerated with zinc diethyldithiocarbamate at 80° C according to T-50-Test and at 70° C according to the quantity of combined sulfur were found to proceed according to zero order kinetics.
- ⁹ Compare Lorenz, D., and Echte, E., loc. cit.⁶ as well as Scheele, W., and Cherubim, M., loc. cit.¹
- ¹⁰ Krebs, H., loc. cit.².
- ¹¹ Scheele, W., Lorenz, O., and Dummer, W., *Kautschuk u. Gummi* **8**, 2 (1955).
- ¹² Zapp, R. L., Decker, R. H., Dyroff, M. S., and Rayner, H. A., *J. Polymer Sci.* **6**, 331 (1950), have published a remarkable experimental work in which they report particularly upon extensive swelling measurements of vulcanizates. Thiuram disulfide and the dithiocarbamate of tetravalent tellurium were the accelerators. The work has kinetic aspects and these were carefully interpreted by Gordon, *J. Polymer Sci.* **7**, 485 (1951), whereby it was proved that sulfur reacts in the initial stage of the vulcanization according to first order kinetics. We see at present no possibility of correlating the work of Zapp and coworkers, and our own results, especially since they made their experiments with butyl rubber.
- ¹³ Scheele, W., and Ilachner-Gensch, C., *Kautschuk u. Gummi* **8**, 55 (1955).
- ¹⁴ Scheele, W., and Gensch, C., *Kautschuk u. Gummi* **6**, 148 (1953).

THE VULCANIZATION OF ELASTOMERS. 17. THE ROLE OF THE OXIDE IN VULCANIZATION WITH THIURAM COMPOUNDS. II *

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INTRODUCTION

Both Craig and coworkers¹ and ourselves^{2,3} have compiled considerable data which contribute to an understanding of thiuram vulcanization. This work sought especially to derive the mechanism of this vulcanization with respect to the chemical properties of thiuram compounds, and it also exhaustively describes the kinetics of the intermediate steps of the reaction. Yet a closer consideration of all the observations indicates, in our opinion, that the situation is much more complicated than at first might be supposed. Thus, as of the present time, thiuram vulcanization cannot be considered as fully explained.

Consequently we continue our research and would like to add now some results to the statements made in the 12th article of this series⁴. We discussed there the formation of an intermediate compound during thiuram vulcanization which must be formed in contact with the zinc oxide, which is recognized as necessary in the vulcanization. In the meantime, we have reported the results of quantitative tests which make the formation of the intermediate compound seem even more certain⁵. While we were engaged in this work, Craig⁶ presented the idea that the formation of zinc dithiocarbamates during thiuram vulcanizations is not uniformly and unavoidably connected with the crosslinking vulcanization reaction, because thiuram disulfide reacts with zinc oxide in absence of rubber, to produce zinc dithiocarbamate. We cannot share this view, because we have been able to show that the crosslinking reaction—as measured by reciprocal equilibrium swelling—proceeds as a first order reaction and at the same rate as the formation of zinc dithiocarbamate. Furthermore, an induction period in the formation of dithiocarbamate during vulcanization of Perbunan by thiuram monosulfide had been shown in reports of some of our work^{4,7} which had not been noted by Craig. The above items of evidence point to the fact that the formation of dithiocarbamate during thiuram vulcanization must be tied in with the crosslinking reaction. However, the observation made by Craig should be carefully checked and investigated. Therefore, we recently announced that we would make a thorough study of the reaction of thiuram disulfide with zinc oxide. This report deals with the results of the work done on this subject and again reviews the kinetics of thiuram disappearance and dithiocarbamate formation as shown by a spectrophotometric method of analysis of the extracts (instead of a conductometric method) so that connection may be made with the work on the chemistry of thiuram vulcanization published by Jarrijon⁸.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe from Kautschuk und Gummi, Vol. 10, pages WT 241 to 250, October 1957. Tables of data have been omitted.

EXPERIMENTAL DATA AND DISCUSSION

The reaction of zinc oxide with tetraethylthiuram disulfide.—ZnO (active) and tetraethylthiuram disulfide were intimately mixed in a mortar, using the molar ratios: TETD:ZnO = 1:10 and 1:3.

Carefully weighed portions of the loosely powdered mixtures were put into test tubes and tamped down as well as possible with a stopper. The powders were brought to reaction at different temperatures in such a way that the

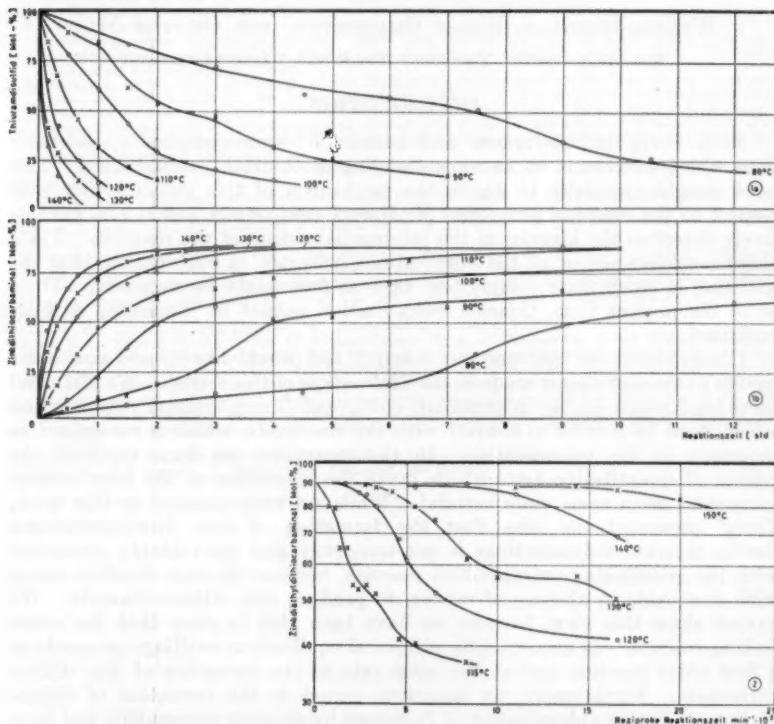


FIG. 1.—Decrease of thiuram disulfide (a) and increase of zinc dithiocarbamate (b) in the reaction of tetraethylthiuram disulfide with zinc oxide (molar ratio TETD:ZnO = 1:10). 1a)—Ordinate: thiuram disulfide (mole %); abscissa: reaction time in hrs. 1b)—Ordinate: zinc dithiocarbamate (mole %); abscissa: reaction time in hrs.

FIG. 2.—Demonstration of the limiting value of zinc dithiocarbamate formation in the reaction of tetraethylthiuram disulfide with zinc oxide (molar ratio TETD:ZnO = 1:3). Ordinate: zinc diethyldithiocarbamate (mole %); abscissa: reciprocal of reaction time, $\text{min}^{-1} \times 10^4$.

reaction time was varied over wide limits. To do this, the test tubes loaded with the mixtures were placed in a thermostat which was set at the desired temperature for reaction. After measured periods of time, samples were removed from the tubes and analyzed for their thiuram disulfide (TETD) and their zinc diethyldithiocarbamate (ZnDED) content. For this purpose, the powders were extracted with benzene which dissolved the remaining thiuram disulfide as well as the ZnDED which had been formed. The extracts, slightly turbid with highly dispersed ZnO, were filtered free of the oxide by

passage through membrane filters. The solvent was then distilled off under vacuum. The residue was taken up in acetone and the solution made up to a definite volume in a volumetric flask. Aliquots of the acetone solution were diluted with water and titrated conductometrically in the usual way⁹.

The results are shown graphically in Figure 1 for mixtures where the molar ratios were TETD:ZnO = 1:10. Figure 1a shows the decrease in thiuram and Figure 1b the increase in dithiocarbamate with time. (The conversions are in mole % of the initial thiuram disulfide.)

The curves do not show the same smooth course that is found in the case of a thiuram vulcanization¹⁰, except at higher temperatures. Especially at 100°, 90° and 80° C the curves for dithiocarbamate formation show a step-like form which—not shown here—is much more pronounced in the results with the molar ratio TETD:ZnO = 1:3 where the formation of dithiocarbamate at 80° C shows three distinct steps. This may be the result of the reaction taking place in the absence of a solvent for the thiuram disulfide and for the zinc dithiocarbamate. We might picture the molecules of the disulfide as reacting on the surface of ZnO crystals and there depositing a layer of the dithiocarbamate, so that further reaction will follow only after diffusion has taken place through a "reaction zone". This may help to make it clear why the reaction proceeds at lower temperatures in steps, or as it were in "periodic" fashion. At higher temperatures, the steps disappear because the diffusion takes place at higher speed. Because of these irregularities which complicate the kinetic relations, we abandoned the possibility of making a simple analysis of the reaction curves and limited ourselves to a more careful consideration of the limiting or ultimate values of the dithiocarbamate formation, which is of prime importance.

The curves, in Figure 1b particularly, show clearly that at elevated temperatures, a limiting value is approached which is substantially higher than is approached in similar curves obtained for this reaction performed in the presence of natural rubber, Buna or Perbunan. Whereas in cases where the polymers are present, 66 mole % of the applied thiuram disulfide is always transformed into zinc dithiocarbamate, regardless of the temperature, in the above cases where rubber is absent, the value is about 90 mole %. This becomes quite apparent if we plot the log of the amount of dithiocarbamate formed against the reciprocal of the reaction time. This is shown in Figure 2 for data obtained with the molar ratio of reactants, TETD:ZnO = 1:3. This shows that in the reaction of zinc oxide with tetraethylthiuram disulfide, 90 mole % of the thiuram disulfide is transformed into ZnDEDC in every case, regardless of the temperature.

This result is surprising; such a high yield would not be expected. Since the dithiocarbamate content of the mixtures was always determined by conductometric titrations with hydrochloric acid of the extracts of the powders, we checked the accuracy and adaptability of this method by repeating the reactions with the mixtures of the molar ratio TETD:ZnO = 1:3 and 1:10, and analyzed the extracts quantitatively through their light absorption spectra in the ultraviolet range. We did this even though the conductometric titration curves were always unobjectionable, and analyses of the extracts for zinc content confirmed the conductometric results. A considerable amount of work had to be done to prepare for the spectrophotometric analysis.

In Figures 3 and 4 we present the UV spectra of ZnDEDC (A) and of TEDC (B) measured in pure methanol at various concentrations (m mole in 1000 ml). The extinction coefficients $A^{m\lambda}$ and $B^{m\lambda}$ are on the ordinates

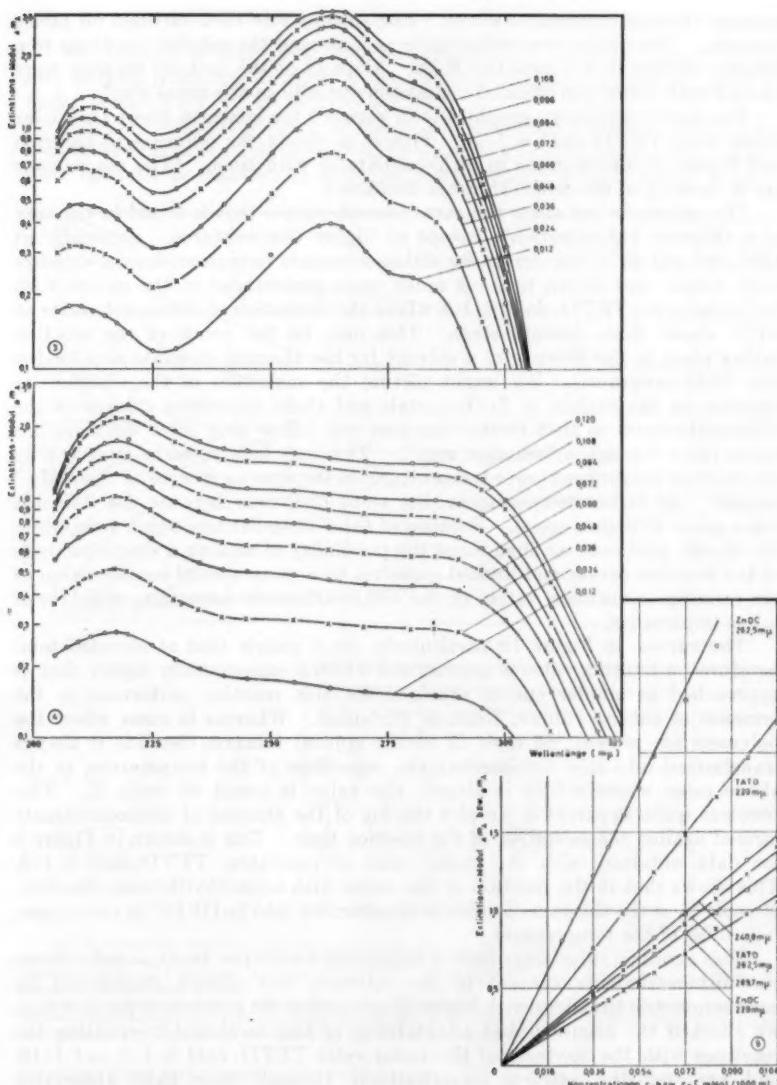


FIG. 3.—Light absorption spectrum (color curves) for zinc diethyldithiocarbamate (A) in methanol at various concentrations. The numbers indicate the concentrations in m mole/1000 ml. Ordinate: extinction coefficient $A^{\text{m}} \lambda$; abscissa: wavelength.

FIG. 4.—Light absorption spectrum (color curves) for tetraethylthiuram disulfide (B) in methanol at various concentrations. The numbers indicate the concentrations in m mole/1000 ml. Ordinate: extinction coefficient $B^{\text{m}} \lambda$; abscissa: wavelength.

FIG. 5.—Dependence of extinction coefficients on concentration in solutions of zinc diethyldithiocarbamate (A) and of tetraethylthiuram disulfide (B) for different wavelengths. (Solutions in ethanol.) The extinction coefficients $A^{\text{m}} \lambda$ or $B^{\text{m}} \lambda$ are:

(logarithmic) and wavelengths in $\mu\mu$ on the abscissae. If the Lambert-Beer Law holds for these color curves of the compounds, we should expect that they could be caused to coincide. A brief inspection shows that this condition is easily met; this also appears clear in Figure 5, in which are shown the calibration curves of tetraethylthiuram disulfide and of ZnDEDCC (extinction coefficients as functions of concentration) for wavelengths 220 and 262.5 $\mu\mu$. The compounds show clear-cut maxima at these wavelengths. The experimental data lie accurately on straight lines.

In Figure 6 are given the spectra of mixtures of TEDC and ZnDEDCC in pure ethanol, with extinction coefficients as ordinates and wavelengths as abscissae.

In every case the total concentration of the reagents was 0.06 m mole per 1000 ml. The molar ratios of the components in the mixture were: TETD:ZnDEDCC = 1:9 and 9:1; 2:8 and 8:2; 3:7 and 7:3; 4:6 and 6:4 and 5:5, or in other words 0.11; 0.25; 0.43; 0.66; 1.0; 1.5; 2.3; 4.0 and 9.0.

The spectra of the solutions of mixtures of TETD and ZnDEDCC show two points of intersection, one at wavelength 289.7, the other at 240.8 $\mu\mu$ with the same extinction coefficients for all mixtures. This is as it should be if the two components in solution have no interaction with each other, or in other words, if the Lambert-Beer Law holds. Since the extinction coefficients for the wavelengths found at the points of intersection of the curves in the spectrophotometric analysis of solutions which contained several proportions of material, will be frequently used, the calibration curves for the wavelengths 289.7 and 240.8 $\mu\mu$ are given in Figure 5.

It is now clear that we can analyze solutions containing both ZnDEDCC and TEDC for each component. The slopes of the graphs in Figure 5 give us the molar extinction coefficients $A^{\epsilon\lambda}$ and $B^{\epsilon\lambda}$ for ZnDEDCC (A) and for TEDC (B) at specific wavelengths. We must also know the extinction coefficients of the solutions, $AB^{m\lambda}$, at two characterizing wavelengths λ_1 and λ_2 in order to analyze solutions for the content of the two components. The following equations, fulfilling the Lambert-Beer law, give the relationship between the concentrations C_A and C_B of zinc diethyldithiocarbamate and tetraethylthiuram disulfide in a common solution of concentration C_{AB} , and the molar extinction coefficients $A^{\epsilon\lambda_1}$ and $B^{\epsilon\lambda_1}$ or $A^{\epsilon\lambda_2}$ and $B^{\epsilon\lambda_2}$, as well as the experimentally measured extinction coefficients of the solutions, $AB^{m\lambda_1}$ and $AB^{m\lambda_2}$ for the wavelengths λ_1 and λ_2 .

$$AB^{m\lambda_1} = C_A \cdot A^{\epsilon\lambda_1} + C_B \cdot B^{\epsilon\lambda_1} \quad (1)$$

$$AB^{m\lambda_2} = C_A \cdot A^{\epsilon\lambda_2} + C_B \cdot B^{\epsilon\lambda_2} \quad (2)$$

The values for C_B in Equations (3) and (4) below are derived from Equations (1) and (2).

$$C_B = \frac{AB^{m\lambda_1} - C_A \cdot A^{\epsilon\lambda_1}}{B^{\epsilon\lambda_1}} \quad (3)$$

$$C_B = \frac{AB^{m\lambda_2} - C_A \cdot A^{\epsilon\lambda_2}}{B^{\epsilon\lambda_2}} \quad (4)$$

Millimolar Extinction Coefficients ϵ

$A^{\epsilon 220.0} = 10.1$; $B^{\epsilon 220.0} = 20.75$

$A^{\epsilon 262.5} = 33.5$; $B^{\epsilon 262.5} = 12.75$

$\epsilon_{240.8} = 13.7$; $\epsilon_{289.7} = 11.8$

Ordinate: extinction coefficients $A^{\epsilon\lambda}$ or $B^{\epsilon\lambda}$; abscissa: concentrations— C_A or C_B (m mole/1000 ml).

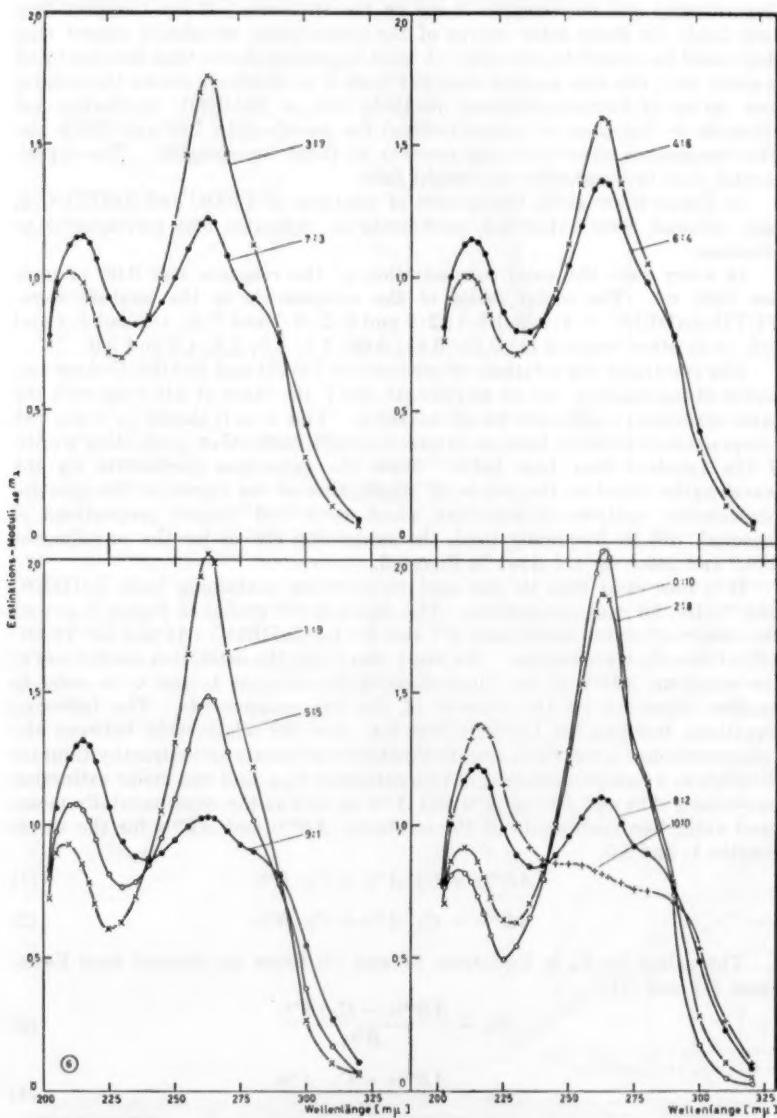


FIG. 6.—Light absorption spectra of solutions which contain both zinc diethyldithiocarbamate and tetraethylthiuram disulfide in various molar proportions, the combined molar concentration being held at 0.06 m mole in 1000 ml. Ordinate: extinction coefficients $AB\lambda$; abscissa: wavelengths ($m\mu$).

TABLE I
SPECTROPHOTOMETRIC ANALYSIS OF SEVERAL METHANOL SOLUTIONS CONTAINING TEDC AND ZnDEDCC IN VARIOUS MOLAR RATIOS. (THE TOTAL CONCENTRATION OF THE TWO REAGENTS WAS HELD AT 0.06 M MOLE/1000 ML.)

		Extinction coefficients $[A_{B\lambda}]$ (averages of three measurements) at wavelengths shown		Concentrations of ZnDEDCC in mole/1000 ml $\times 10^6$ (C_A) calculated by Equation 6 from the extinction coefficients $[A_{B\lambda}]$ and the molar extinction coefficients $[A_{T\lambda}]$ and $[A_{D\lambda}]$ for wavelength shown		Average values for C_A from a, b, c		C_A in %	Concentration of ZnDEDCC in %	C_A in %	Concentration of TEDC in %	C_A in %	Dium of ZnDEDCC and TEDC in %	
a	b	$\lambda_1 = 262.5 \text{ m}\mu$	$\lambda_2 = 262.5 \text{ m}\mu$	$\lambda_1 = 240.8 \text{ m}\mu$	$\lambda_2 = 240.8 \text{ m}\mu$	$\lambda_1 = 298.7 \text{ m}\mu$	$\lambda_2 = 298.7 \text{ m}\mu$	$\lambda_1 = 262.5 \text{ m}\mu$	$\lambda_2 = 262.5 \text{ m}\mu$	$\lambda_1 = 220.0 \text{ m}\mu$	$\lambda_2 = 220.0 \text{ m}\mu$	$\lambda_1 = 220.0 \text{ m}\mu$	$\lambda_2 = 220.0 \text{ m}\mu$	
10: 0	1.983	0.712	0.806	0.610	599.0	608.5	606.6	604.7	549.9	543.7	58.7	100.8	—	
9: 1	1.869	0.740	0.804	0.671	527.9	553.3	549.9	543.7	—	—	90.6	9.8	100.4	
8: 2	1.742	0.703	0.732	0.732	489.7	488.8	487.8	487.8	—	—	81.3	19.2	100.5	
7: 3	1.615	0.692	0.809	0.796	428.1	425.6	425.6	426.4	425.6	426.4	76.1	71.1	29.3	
6: 4	1.495	0.699	0.810	0.862	365.0	365.7	365.1	365.3	365.0	365.3	237.6	60.9	39.6	
5: 5	1.365	0.695	0.806	0.921	297.9	298.5	302.8	299.7	298.0	298.0	298.0	49.9	49.7	
4: 6	1.238	0.708	0.810	0.994	233.4	238.9	238.2	236.8	233.4	233.4	236.8	39.5	60.6	
3: 7	1.125	0.708	0.812	1.059	177.5	182.2	180.9	180.2	180.9	180.2	180.2	422.7	30.0	
2: 8	0.998	0.702	0.809	1.122	118.1	120.8	118.5	119.1	118.1	118.5	118.5	482.7	19.9	
1: 9	0.875	0.699	0.808	1.183	58.9	60.6	58.1	59.2	58.9	58.1	58.1	541.2	9.9	
0:10	0.756	0.696	0.805	1.240	0.6	3.2	0.6	0.6	0.6	0.6	0.6	507.3	0.2	99.6

from which we derive:

$$(AB^{m\lambda_1} - C_A \cdot A^{\epsilon\lambda_1})B^{\epsilon\lambda_2} = (AB^{m\lambda_2} - C_A \cdot A^{\epsilon\lambda_2})B^{\epsilon\lambda_1} \quad (5)$$

$$C_A = \frac{AB^{m\lambda_1} \cdot B^{\epsilon\lambda_2} - AB^{m\lambda_2} \cdot B^{\epsilon\lambda_1}}{A^{\epsilon\lambda_1} \cdot B^{\epsilon\lambda_2} - A^{\epsilon\lambda_2} \cdot B^{\epsilon\lambda_1}} \quad (6)$$

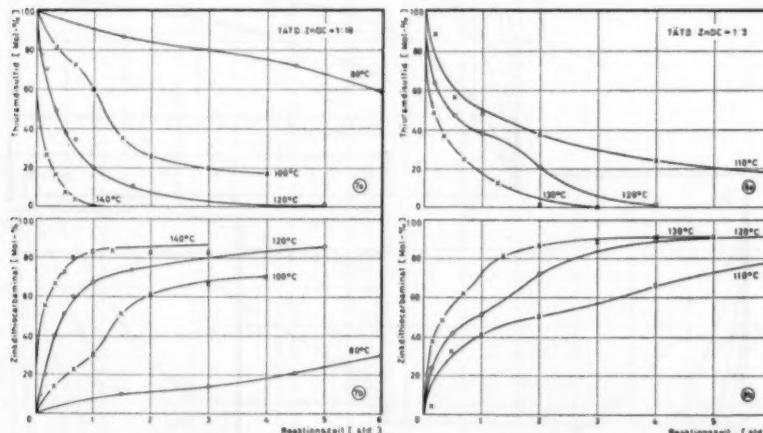
The concentration C_B is then calculated by substituting C_A in Equation (3) or (4).

We convinced ourselves of the applicability of this procedure to our problem by a series of control experiments. The spectrophotometric tests of the solutions defined in column 1 of Table I, at wavelengths $\lambda_1 = 262.5$; $\lambda_2 = 289.7$; $\lambda_3 = 240.8$; $\lambda_4 = 220.0 \text{ m}\mu$, gave the extinction coefficients shown in columns 2 to 5 of Table I. Of these values, those given for wavelengths 289.7 and 240.8 $\text{m}\mu$ are practically constant, since the combined (total) concentration of the reagents in the solutions was constant at 0.06 m mole in 1000 ml of methanol (intersection points of the curves). By substitution in Equation (6) of the values found at the pairs of wavelengths given at the heads of columns 6 to 8, the values of the concentrations of ZnDEDCC in m moles per 1000 ml, as given in columns 6 to 8 were calculated. These values are in good agreement, so their averages are tabulated in column 9. Using these values and the extinction coefficients measured at 220 $\text{m}\mu$ the thiuram contents of the solutions were calculated by means of Equation (4) using $\lambda_2 = \lambda_4 = 220 \text{ m}\mu$. These values are listed in column 10. Finally, the per cent of ZnDEDCC and of TETD are given in columns 11 and 12, respectively, and the sums of the percentages of the two materials are given in column 13. These values indicate that the spectrophotometric method of analysis is sufficiently accurate.

The reaction of TEDC with ZnO was again investigated, using the spectrophotometric method of analysis and with mixtures of the same molar ratios as used before, viz. TETD:ZnO = 1:10 and 1:3. The extinction coefficients for wavelengths 262.5, 289.7, 240.8 and 220.0 $\text{m}\mu$ were established as in the control experiments of Table I, by calculations of the dithiocarbamate content of the powders. The calculations were carried out by substitution in Equation (6) of the respective values for the wavelength pairs 262.5 and 289.7; 262.5 and 240.8; 262.5 and 220.0 $\text{m}\mu$. Averages were taken of the three values obtained with the above pairs; the values taken toward the end of the reaction were always in good agreement. The results of spectrophotometric analyses of methanol extracts of the powders are shown graphically in Figures 7 and 8. (Ordinates are, respectively, TETD or ZnDEDCC in mole %, and abscissae are reaction times in hours).

Without further demonstration it may be said that close inspection of reaction curves in Figures 7b and 8b, emphasizes the fact that the spectrophotometric method of analysis also indicates that the limiting value for dithiocarbamate formation is 90 per cent of the initial TEDC. In spite of this agreement between the conductometric and photometric methods of analysis as to the final yield of ZnDEDCC the two methods show discrepancies in the results along the reaction curves, differences which are beyond the limits of accuracy, and which become smaller and smaller toward the end of the reaction. With unreacted powder mixtures, the spectrophotometric method gives higher values for the dithiocarbamate content than does the conductometric method. This leads us to infer that we have to deal with at least one unknown compound when we are working with extracts from incompletely reacted mixtures. This

compound exists in the intermediate stages, but is not present toward the end of the reaction, and is not detected by the conductometric method but is shown in the spectrophotometric method. This occasions a discrepancy between the methods and is a matter for further research. As for the present state of our knowledge of the reaction of oxide in thiuram vulcanizations, the very essential feature persists, that both the conductometric and the spectrophotometric methods of analysis show the limiting value for ZnDEDCC formed from the reaction of zinc oxide with TEDC to be 90 mole % of the initial thiuram disulfide, and that this is independent of temperature. We must then conclude that in the case of thiuram vulcanization, in which the limiting value for ZnDEDCC formed is consistently 66 mole %, some other circumstances must exist, and that the rubber is not without influence on the ZnDEDCC formation.



Figs. 7 and 8.—Spectrophotometric analysis of decrease in tetraethylthiuram disulfide (a) and increase in zinc diethyldithiocarbamate (b) in the reaction of tetraethylthiuram disulfide with zinc oxide. Molar ratios in the reaction mixtures: TETD:ZnO = 1:10 in 7a and 7b and 1:3 in 8a and 8b. Ordinate: thiuram disulfide (mole %) in 7a and 8a and zinc diethyldithiocarbamate (mole %) in 7b and 8b; abscissa: reaction times in hrs.

This is in agreement with facts which we have earlier introduced. We wish to support the theory which we have elsewhere advanced⁴, of an intermediate interference of the rubber in the dithiocarbamate formation with simultaneous crosslinking of the rubber during thiuram vulcanization.

Spectrophotometric analysis in thiuram vulcanization.—Although it should be assumed from the foregoing data, that a spectrophotometric analysis in the case of a thiuram vulcanization would give us nothing more than a conductometric mass analysis has already brought to light, yet, in order to round out the state of our knowledge, we renewed our investigations, in a large way, of the kinetics of thiuram vulcanization, by analyzing the extracts of vulcanizates spectroscopically in the manner described above. The calculations of dithiocarbamate content by Equation (6) were made only with the data for the wavelength pairs 262.5 and 240.8 as well as 262.5 and 220.0 μ . Examination of the experimental data for 289.7 μ showed important deviations from the other individual results. At the present time we frankly can give no explanation for these deviations.

The results obtained for experiments in the temperature range 100° to 150°C are shown graphically in Figures 9 and 10. (Ordinates are thiuram disulfide or zinc dithiocarbamate in mole %; abscissae are vulcanization times in hours.) It is easily seen that the reaction curves show the same form as that shown by the curves for the conductometric analysis of vulcanizate extracts; it is also clear that the dithiocarbamate content approaches the limiting value of 66 mole % based on the initial thiuram disulfide. This is

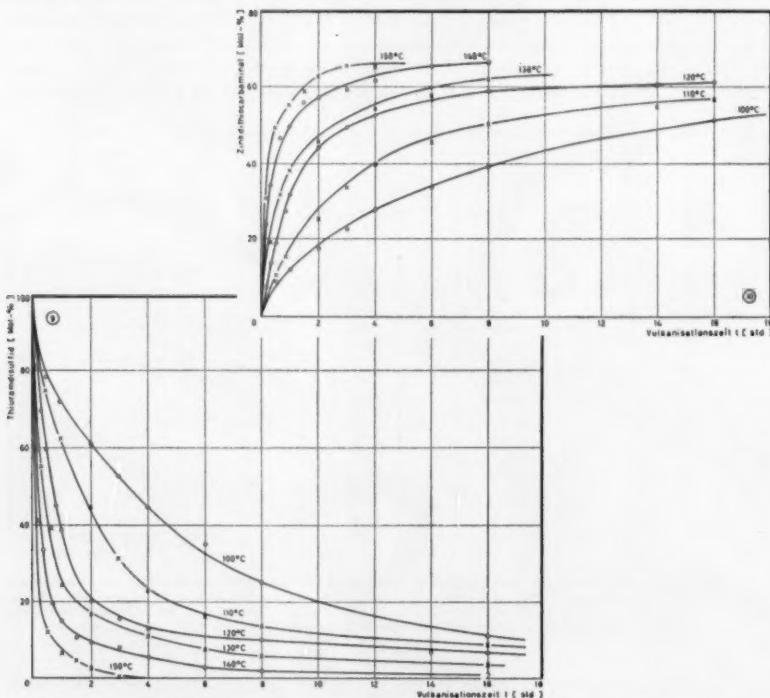


FIG. 9.—Spectrophotometric analysis of the decrease in tetraethylthiuram disulfide in the vulcanization of natural rubber in presence of 2.96 g TETD and 5 g ZnO in 100 g of compound. Ordinate: thiuram disulfide (mole %); abscissa: vulcanization time (hrs).

FIG. 10.—Spectrophotometric analysis of increases in zinc diethyldithiocarbamate in the vulcanization of natural rubber with tetraethylthiuram disulfide (2.96 g TETD and 5 g ZnO in 100 g of compound). Ordinate: ZnDEDC (mole %); abscissa: vulcanization time (hrs).

shown particularly well in Figure 11 where the log of dithiocarbamate content is plotted against the reciprocal of the vulcanization time. A spectrophotometric analysis of dithiocarbamate formed during thiuram vulcanization has also been carried out by Jarrijon, who in this way came to the conclusion that there is a three-fourths transformation of thiuram disulfide to dithiocarbamate⁸. He also commented to us, that in his dissertation¹¹ he had also found a limiting value of 66 mole % for the dithiocarbamate formed. All in all, then we may say that there is an excellent agreement between our experimental results and those of Jarrijon, who was the first to emphasize the constant

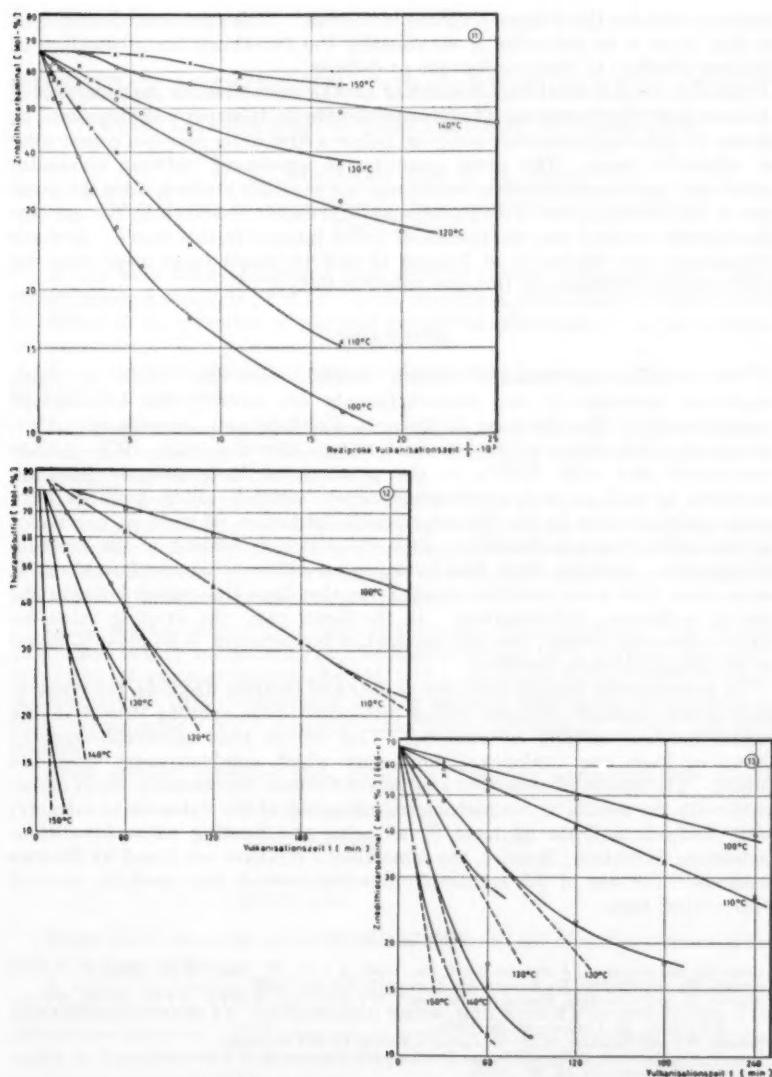


Fig. 11.—Demonstration of limiting value of dithiocarbamate formation in the vulcanization of natural rubber with tetraethylthiuram disulfide, shown by spectrophotometric analysis. Ordinate: ZnDEDCA (mole %); abscissa: reciprocal of vulcanization time [$(1/t) \cdot 10^4$].

Fig. 12.—Decrease of concentration of tetraethylthiuram disulfide as a first order reaction in the vulcanization of natural rubber; evidence by spectrophotometric analysis. Ordinate: thiuram disulfide (mole %); abscissa: vulcanization time (min).

Fig. 13.—Dithiocarbamate formation as a first order reaction in the vulcanization of natural rubber with tetraethylthiuram disulfide in presence of zinc oxide; results by spectrophotometric analysis. Ordinate: ZnDEDCA (mole %) (66.6-x); abscissa: vulcanization time (min).

limiting value for the dithiocarbamate formation. This agreement is sufficient so that there is no reflection if we consider the two-thirds transformation of thiuram disulfide to dithiocarbamate as definite.

Finally, we point out that Figures 12 and 13 show that the consumption of thiuram and the formation of dithiocarbamate in thiuram vulcanization, as shown by spectrophotometric analysis, follow a first order reaction course over an extensive range. The exact quantitative agreement between conductometric and spectrophotometric results was not carefully studied, since the question of the limiting value of dithiocarbamate formation as shown by the spectrophotometric method was the feature of prime interest in this paper. A closer explanation and discussion of Figures 12 and 13 would make clear what we have already published on thiuram vulcanization.

SUMMARY

The reaction of tetraethylthiuram disulfide with zinc oxide, in which significant amounts of zinc dithiocarbamate are formed, was investigated quantitatively. The decrease in thiuram disulfide and increase in dithiocarbamate were followed by conductometric titration with HCl (dithiocarbamate) and with CuSO₄ in the presence of hydroquinone (thiuram disulfide) as well as by a spectrophotometric method. Both methods gave as the limiting value for the dithiocarbamate formation, 90 mole %, calculated on the initial thiuram disulfide. This value is independent of the reaction temperature. Judging from this evidence on dithiocarbamate formation, it seems clear that some condition holds here other than that which holds in the case of a thiuram vulcanization. In the latter case, the limiting value for dithiocarbamate formed, also independent of temperature, is 66 mole % based on the initial thiuram disulfide.

In incompletely reacted mixtures of ZnO and thiuram disulfide, the spectrophotometric method indicates higher dithiocarbamate content than does the conductometric method of analysis. This shows that spectrophotometry shows at least one (unknown) compound which conductometry does not detect. The spectrophotometric analyses of thiuram vulcanizates are in agreement with the results of conductometric titrations of the vulcanizate extracts; both methods indicate 66 mole % as being the limiting value for dithiocarbamate formation; likewise, the same kinetic relations are found by the two methods. The use of the spectrophotometric method was carefully checked with control tests.

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THE HEAT AGING OF NATURAL RUBBER VULCANIZED WITH TETRAMETHYLTHIURAM DISULFIDE *

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It has long been recognized that natural rubber vulcanized with tetramethylthiuram disulfide (TMTD) in the absence of added sulfur is outstanding in respect of its retention of physical properties after aging in air at elevated temperatures.

Two recent investigations have produced data bearing on this superiority of TMTD vulcanizates:

1. Scheele and coworkers¹ have shown that in the course of the vulcanization of such compounds, two-thirds of the TMTD is converted into zinc dimethylthiocarbamate (ZnDMDC).

2. Dunn and Scanlan², by measurements of stress relaxation in air at elevated temperature, have demonstrated that a wide range of dithiocarbamates, including the zinc salts, produce a considerable retardation in the degradation of acetone extracted TMTD crosslinked rubber, although such protection is not afforded to sulfur/accelerator vulcanizates.

Quite apart from any differences in the rates of degradation of TMTD and sulfur/accelerator vulcanizates attributable to differences in network structure², the above facts suggest that the ZnDMDC formed *in situ* during TMTD vulcanization may be partly responsible for the superior heat aging performance of such vulcanizates. This possibility has been investigated in the following manner.

From acetone extracted pale crepe the following compound was mixed:

PURE GUM COMPOUND

Extracted crepe	100
TMTD	3.0
Zinc oxide	2.0
Stearic acid	1.0

Three sheets were vulcanized for 40 minutes at 140° C and subjected to the following treatments:

A, control untreated; B, acetone extracted (to remove ZnDMDC); C, acetone extracted, followed by incorporation of 2.55 phr ZnDMDC by swelling from chloroform solution. This concentration of the ZnDMDC corresponds to that which is formed in the compound, during vulcanization, by transformation of two-thirds of the TMTD content.

Visual examination of the pure gum samples after aging at 100° C showed striking differences. The extracted specimens were largely resinified and brittle, whereas the control and the vulcanizate to which ZnDMDC had been added were still rubbery. Quantitative measurements could not be obtained with pure gum stocks due to the high incidence of breaks in the aged test

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pieces at or adjacent to the grips. For this reason further experiments were carried out on a black reinforced compound having the following formula:

BLACK COMPOUND

Acetone extracted masterbatch (Pale crepe 100; Philblack A 50)	150
TMTD	3
Stearic acid	2.0
Zinc oxide	2.0

Vulcanizates treated as in A, B, and C were again prepared. Tensile strength, modulus and elongation measurements were made upon these three treatments before and after aging for various times at 100° C, in accordance with BS 903: 1956 (part A.19 method B).

The results are given in the table below.

AGING OF BLACK REINFORCED TMTD STOCKS

Sample		Control	Dithiocarbamate removed	Dithiocarbamate replaced
Unaged	TS	215	214	192
	EB	390	370	370
	M100	24	26	25
Aged 1 day at 100° C	TS	164	150	145
	EB	315	320	295
	M100	28	25	26
Aged 3 days at 100° C	TS	125	43	99
	EB	290	380	285
	M100	19	4	16
Aged 5 days at 100° C	TS	112	7	67
	EB	275	180	275
	M100	19	5	14
Aged 7½ days at 100° C	TS	111	19	36
	EB	280	15	290
	M100	20	—	7

TS = tensile strength, kg/cm².

EB = elongation at break %.

M100 = modulus at 100% elongation, kg/cm².

CONCLUSIONS

Acetone extraction of the TMTD stock, which is known to remove the ZnDMDC formed during vulcanization, also leads to a reduction in heat aging resistance. Addition to the extracted vulcanizate of the appropriate quantity of ZnDMDC from a solution improves the aging behavior although not to the level of the untreated vulcanizate.

This failure to restore in full the aging resistance of the initial stock by swelling in the appropriate quantity of ZnDMDC is hardly surprising since it is likely that the ZnDMDC will be present in the original and in the dosed vulcanizate in somewhat different physical forms and distributions.

The results demonstrate that the dithiocarbamate formed *in situ* during TMTD vulcanization plays a major part in conferring heat resistance to such vulcanizates.

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² Dunn, J. R., and Scanlan, J., *J. Polymer Sci.* (in press).

THE ACTION OF VULCANIZATION ACTIVATORS *

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In modern vulcanization technology metal oxides are widely used as vulcanization activators, especially zinc oxide. Vulcanization activators substantially improve the vulcanization process and the quality of the vulcanizates. However, despite the extensive technical use of activators the mechanism of their action is not sufficiently well understood and the experimental data and the theoretical considerations of various authors in the literature are often contradictory.

The most widely accepted view of the role of vulcanization activators is based on their comparison with promoters in catalytic reactions. It is also believed¹ that metal oxides and accelerators, and in particular mercaptans and dithiocarbamic acids, form saltlike compounds which owing to their better solubility produce high accelerator activity. According to Bruni and Romani², and also to Bedford and Sebrell³, these saltlike compounds react with sulfur to form di- or polysulfides, which evolve sulfur in an active form. Recently it has been shown⁴ that zinc oxide participates in reactions which lead to the formation of the vulcanizate spatial network. This aspect of the problem, which is of great theoretical and practical interest, requires further study.

EFFECT OF ZINC OXIDE AND STEARIC ACID ON THE KINETICS OF THE ADDITION OF SULFUR TO SKB RUBBER

The kinetics of the addition of sulfur to rubber was studied in mixtures based on sodium butadiene rubber (SKB) with the following primary composition (in parts by weight): SKB 100, sulfur 3, and phenyl-2-naphthylamine (PBNA) 2. To this basic composition, the necessary amounts of the other components were added: zinc oxide, stearic acid, and accelerators: mercapto-benzothiazole (MBT) and diphenylguanidine (DPG). The mixing was carried out on microrollers in air; the vulcanization was carried out in a press. Combined sulfur was determined by oxidation of the vulcanizate by a mixture of nitric acid and bromine in presence of magnesium oxide. The ZnS content of parallel samples of the vulcanizates was determined by the amount of H₂S evolved from the sample swollen in ether by the action of concentrated hydrochloric acid in a current of nitrogen. The difference between the total bound sulfur and the sulfur contained in the vulcanizate as ZnS gives the "organic bound sulfur", or the sulfur combined direct with the rubber. The curves shown in this paper represent the kinetics of the addition of organic bound sulfur in contrast to most published papers on vulcanization kinetics where bound sulfur is taken to mean all the sulfur which is not extracted from the vulcanizate by acetone, including the sulfur contained in the vulcanizate as zinc sulfide. This incorrect method of determination can lead to erroneous conclusions.

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The technical SKB used contained 0.56-0.67 per cent alkali calculated as Na_2CO_3 . As alkali accelerates the sulfur addition reaction, in order to eliminate this effect some of the experiments were carried out with specially purified rubber, from which the alkali was removed by a method developed by A. V. Dobromyslova (by heating with stearic acid and removal of sodium stearate by precipitation of the rubber from benzene solution by methyl alcohol).

As a rule, metal oxides are added to the vulcanization mixture together with fatty acids, usually with stearic acid. It is believed that the activating action of zinc oxide is fully effective only in presence of this acid. Therefore

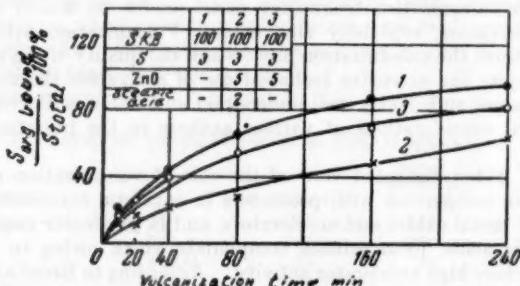


FIG. 1.—Kinetics of sulfur addition in mixtures based on technical sodium butadiene rubber (SKB) without accelerator. The composition is given in parts by weight.

in our experiments we investigated the action of zinc oxide both separately and together with the generally used amount of stearic acid (2 per cent on the weight of the rubber).

Figure 1 represents the kinetics of sulfur addition in mixtures of technical SKB without accelerator. It is seen that in the presence of zinc oxide (5 parts by weight on the rubber) the rate of sulfur addition is somewhat retarded. A greater retardation occurs by the combined action of zinc oxide and stearic acid. The intensification of the retardation effect in the addition of sulfur to

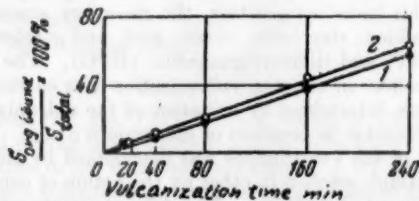


FIG. 2.—Kinetics of the addition of sulfur to purified sodium butadiene rubber; composition of mixtures as in Figure 1.

rubber by the action of stearic acid may in this case be probably ascribed to neutralization of the alkali contained in the rubber which, as has already been stated, accelerates the addition of sulfur to rubber. In fact, as Figure 2 shows, a binary mixture of purified alkali-free rubber and sulfur vulcanizes very slowly; zinc oxide and stearic acid have practically no effect on the rate of sulfur addition (the data in Figure 2 indicate a slight acceleration, which may be attributed to bad reproducibility of the results, largely owing to imperfect mixing of the components).

In mixtures with technical SKB containing MBT as accelerator, zinc oxide substantially lowers the rate of sulfur addition (Figure 3). In the presence of stearic acid, and also of stearic acid and zinc oxide, the rate of sulfur addition is practically equal to the vulcanization rate of the original mixture. Since, as was stated earlier, stearic acid neutralizes the alkali in technical rubber, it is evident that stearic acid exerts an accelerating effect in mixtures with MBT.

In mixtures containing DPG as accelerator, zinc oxide and stearic acid do not change the rate of sulfur addition.

The retarding effect of zinc oxide in the vulcanization of mixtures containing mercaptobenzothiazole is primarily caused by the formation of zinc mercaptide which, contrary to Auerbach's views⁴, is, according to our data and the results of others⁵, a less active accelerator of the addition of sulfur to rubber than MBT. In addition, the presence of ZnO in the system leads to a number of reactions which are described below, in which zinc sulfide is formed and which therefore lower the content of organic bound sulfur.

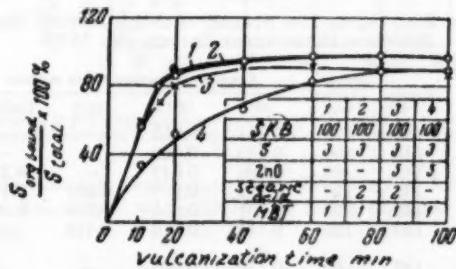


FIG. 3.—Kinetics of sulfur addition in mixtures of SKB rubber containing MBT as accelerator.

The accelerating action of stearic acid in mixtures with MBT requires special study. As will be shown later in this paper, stearic acid substantially increases the rate of isotope exchange between MBT and elementary sulfur. In addition, it was shown in our experiments carried out jointly with I. A. Tutorskii that stearic acid reacts at 140° with MBT with evolution of hydrogen sulfide. These reactions are probably the cause of the activating effect of stearic acid reacts at 140° with MBT with evolution of hydrogen sulfide. These reactions are probably the cause of the activating effect of stearic acid in the addition of sulfur to rubber in the presence of mercaptobenzothiazole.

Thus, the experimental data show that in the sodium butadiene rubber mixtures studied zinc oxide does not accelerate the addition of sulfur to rubber and so cannot be regarded as an "activator" of vulcanization. This is in agreement with the results of the experiments carried out by Dogadkin, Feldshtein, and Orlovskii⁶, who showed, however, that the role of zinc oxide (as of other metal oxides) greatly depends on the type of rubber and of accelerator, and of the type of carbon black used as filler.

EFFECT OF ZINC OXIDE AND STEARIC ACID ON ISOTOPE EXCHANGE BETWEEN ELEMENTARY SULFUR (S^{35}) AND THE THIOL GROUP SULFUR IN MERCAPTOBENZOTHIAZOLE

The view has been recently put forward in a number of papers⁶ that vulcanization reactions and isotope exchange reactions between sulfur and the

accelerator have a common mechanism. In this connection it was of some interest to study the influence of vulcanization accelerators on isotope exchange of sulfur with the accelerator studied—mercaptobenzothiazole. The experiments were carried out both in molten sulfur and in a solution in vaseline oil with the aid of a technique similar to that described by Guryanova⁶. The results are shown in Table I. The results show that zinc oxide sharply retards and decreases the extent of exchange of S³⁵ with MBT, while stearic acid has a considerable activating effect on the process. Thus, the influence of ZnO and stearic acid on the exchange reaction is analogous to their influence on the addition of sulfur to rubber in the presence of MBT as vulcanization accelerator. We do not incline to the view that vulcanization reactions consist only of the reactions which occur in the exchange of sulfur with the accelerator⁷, but nevertheless it is a significant fact that stearic acid exerts an independent and special action in comparison with zinc oxide both in the addition of sulfur to rubber

TABLE I
EFFECT OF ZINC OXIDE AND STEARIC ACID ON ISOTOPE EXCHANGE
BETWEEN ELEMENTARY SULFUR AND MBT

Experimental conditions	Temp., °C	Heating time, min	Content of components in mixture				Exchange, % of equilibrium
			S ³⁵	MBT	ZnO	C ₁₈ H ₃₄ O ₂	
Melt	145	120	0.094	0.055	—	—	73.2
	145	300	0.133	0.062	—	—	90.5
	145	80	0.099	0.049	—	0.227	80.0
	145	120	0.132	0.069	0.264	0.110	1.1
	145	300	0.101	0.055	0.251	0.101	5.6
	150	120	0.144	0.076	0.473	—	6.0
Solution in vaseline oil	143	80	0.115	0.056	—	—	30.0
	143	80	0.123	0.056	—	—	90.0
	143	80	0.109	0.057	0.029	0.011	12.7

and in the exchange reaction of sulfur with MBT. This means that stearic acid (and probably other fatty acids) should not be regarded as only a dispersing agent or solvent for zinc oxide, as is usually stated in the technical literature on vulcanization. Apparently it takes direct part in vulcanization, and reacts with the accelerator and the other components of the vulcanization mixture.

FORMATION OF ZINC SULFIDE IN THE VULCANIZATION OF SODIUM BUTADIENE RUBBER

In the vulcanization of rubber mixtures containing zinc oxide, part of the sulfur is combined as zinc sulfide. Figure 4 shows the kinetics of ZnS formation in the vulcanization of mixtures containing MBT and DPG as accelerators, and it is seen that in the initial stages of vulcanization zinc sulfide is formed more rapidly in mixtures with MBT than in mixtures with DPG.

Figure 5 represents the relationship between the amount of ZnS formed and the content of organically bound sulfur. As was already shown by Hull, Weinland, Olsen, and France⁴, the relative content of sulfur in the form of zinc sulfide is higher in vulcanizates without accelerator than in vulcanizates containing MBT and DPG as accelerators. It is also seen that in the last stage of the process (beyond the vulcanization optimum) mixtures with MBT show a sharp increase of the ZnS:S_{bound} ratio, which indicates the formation of ZnS as the result of reactions with participation of sulfur already combined with the rubber.

The kinetics of ZnS formation and the dependence of the amount of zinc sulfide formed on the composition of the vulcanization mixture indicate that this substance is formed as the result of a series of reactions. It was therefore of interest to find the reactions which may lead to ZnS formation in vulcanization conditions.

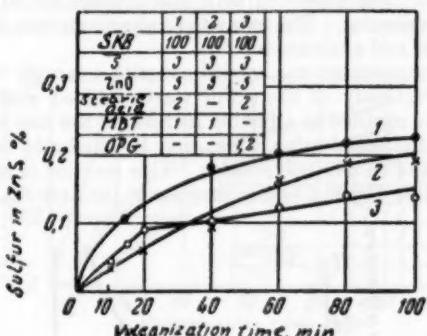
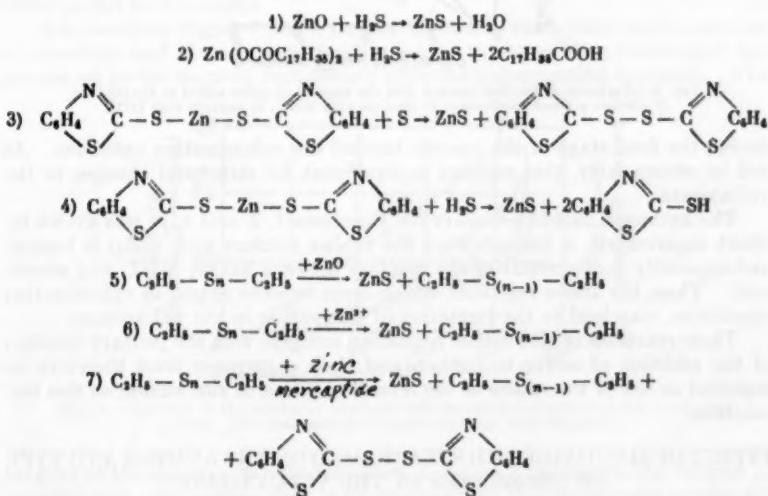


FIG. 4.—Kinetics of ZnS formation in mixtures with SKB rubber containing MBT or DPG as accelerators: the amount of ZnS is expressed as the S content in % of the bound sulfur.

It was experimentally shown that zinc sulfide may be formed in the following reactions: Reaction 1 was carried out in an aqueous medium, and the others in xylene.



Reactions 1 and 2 proceed at a high rate at room temperature. Reaction 3 (with zinc mercaptide) proceeds slowly at vulcanization temperature (143°); Reaction 4 is fairly rapid in the same conditions. Reactions 5, 6, and 7 correspond to reactions of rubber polysulfides with zinc oxide and zinc salts;

they proceed fairly slowly at vulcanization temperature (in 1 hour \sim 50% of the reacting quantity of diethyl polysulfide is decomposed).

The possibility of zinc sulfide formation as the result of secondary reactions between zinc oxide and rubber polysulfides was also established by direct experiments. For this, a mixture containing MBT as accelerator was vulcanized for 20 minutes and then extracted with cold acetone for 50 hours to remove free sulfur and accelerator. The extracted vulcanize was then heated again at 142° for 2 hours and analyzed for ZnS.

An analogous experiment was carried out with a sample vulcanized for 100 minutes, when practically all the sulfur was combined with the rubber. In both cases, heating resulted in a further increase of the zinc sulfide content by 32–36 per cent of the initial value, which may be attributed to the reaction between zinc oxide and rubber polysulfides. This reaction is responsible for the previously noted (see Figure 5) sharp increase of the $ZnS:S_{\text{bound}}$ ratio observed

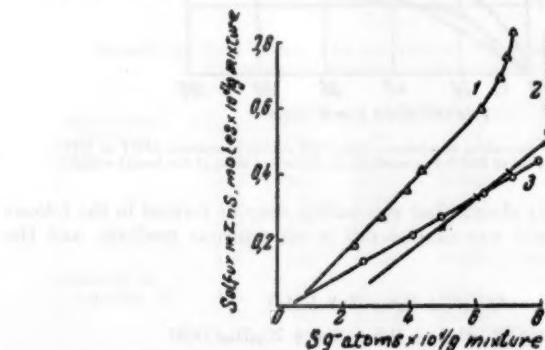


FIG. 5.—Variation of the ZnS content with the amount of sulfur added to the rubber:
1) mixture without accelerator; 2) mixture with MBT; 3) mixture with DPG.

during the final stage of the process beyond the vulcanization optimum. As will be shown later, this reaction is significant for structural changes in the vulcanizate.

The hydrogen sulfide necessary for Reactions 1, 2, and 4, as was shown by direct experiments, is formed when the rubber mixture with sulfur is heated, and especially as the result of the reaction between sulfur, MBT, and stearic acid. Thus, the above reactions, which occur to some extent in vulcanization conditions, may lead to the formation of zinc sulfide in the vulcanizate.

These reactions of zinc sulfide formation compete with the primary reaction of the addition of sulfur to rubber, and their occurrence must therefore be regarded as one of the causes of the retarding action of zinc sulfide on this last reaction.

EFFECT OF ZINC OXIDE AND STEARIC ACID ON THE NUMBER AND TYPE OF CROSSLINKS IN THE VULCANIZATE

It follows from the above experimental data that in sodium butadiene rubber mixtures ZnO does not accelerate, but in some cases retards, the addition of sulfur to rubber. Nevertheless, it is known from technological practice that vulcanizates with good technical properties can in most cases be obtained only by the use of zinc oxide or other metal oxides. This leads to the conclu-

sion that zinc oxide has a significant effect on another aspect of the vulcanization process—the number and nature of crosslinks between the molecular rubber chains⁴.

For determination of this aspect of the action of vulcanization activators, the number of crosslinks was determined with the aid of the Flory-Rehner equation from the swelling maximum of the vulcanizates. As is seen from Figure 6, zinc oxide alone in mixtures containing mercaptobenzothiazole does

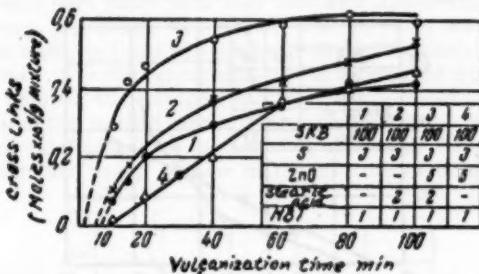


FIG. 6.—Kinetics of crosslink formation during vulcanization of sodium butadiene rubber.

not accelerate crosslinking of the rubber molecules; a sharp acceleration is found with the combined action of zinc oxide and stearic acid. The positive action of activators on the formation of the space structure of vulcanizates is seen more clearly by a comparison of the number of crosslinks with the amount of sulfur added to the rubber.

It is seen from Figure 7 that a linear relationship exists between the number of crosslinks and the amount of sulfur added to the rubber throughout the process up to the moment immediately after the vulcanization optimum. The

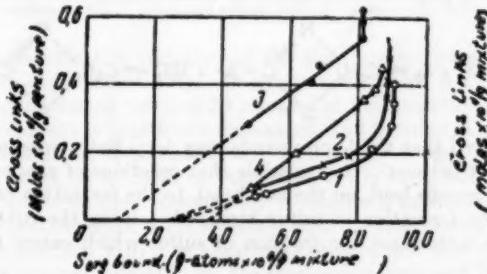


FIG. 7.—Variation of the number of crosslinks with the amount of sulfur combined with the rubber. The compositions of the mixtures are as in Figure 6.

tangent of the slopes of the straight lines in Figure 7 represents the "degree of crosslinkage", and a comparison of the angles shows that stearic acid accelerates sulfur addition without increasing the fraction of the sulfur which enters the crosslinks. The "degree of crosslinking" increases sharply on the introduction of ZnO into the mixture. This shows that the essential role of zinc oxide as a vulcanization activator consists of the fact that in the presence of ZnO the fraction of the sulfur used for crosslink formation in the vulcanizate increases;

and it is known that crosslink formation is the essential feature of the vulcanization process.

In mixtures containing DPG as accelerator, the role of zinc oxide is less prominent. In this instance ZnO increases the "degree of crosslinking" only during the second part of the vulcanization process (Figure 8). A comparison of Curve 1, Figure 7 with Curve 1, Figure 8 shows that in mixtures without vulcanization activators (ZnO and stearic acid) diphenylguanidine causes a greater crosslinking effect than mercaptobenzothiazole.

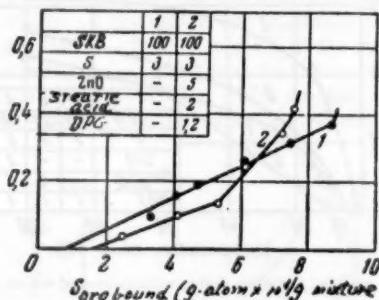
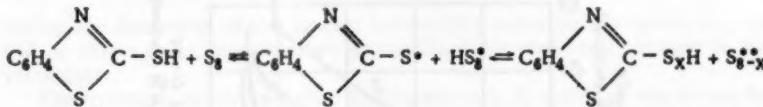


FIG. 8.—Variation of the number of crosslinks with the amount of sulfur combined with the rubber.

The formation of sulfur crosslinks between the rubber molecules in the vulcanizate occurs as the result of a number of chemical reactions. On the basis of our experimental data the following possibilities for the participation of zinc oxide in these reactions, affecting the extent of crosslinking, may be considered.

a) The reaction of mercaptobenzothiazole with sulfur occurs through the formation of thiol polysulfide compounds⁸ according to the scheme:



Naylor⁹ showed that thiol compounds may form both crosslinks and intramolecular ring structures. It is possible that reactions of zinc oxide and zinc salts with thiol groups lead, on the one hand, to the formation of ZnS, and on the other, to the formation of sulfur biradicals joining the rubber molecular chains. In the latter case the fraction of sulfur which enters the crosslinks increases.

b) According to the views of a number of workers¹⁰, thiol groups are formed in the molecular chains of rubber during vulcanization, as the result of reactions between sulfur and α -methylene groups, or of addition of H_2S or HS^{\bullet} at the double bonds. The thiol groups are then oxidized by sulfur (Fisher) or by zinc oxide (Armstrong) to form disulfide crosslinks between the rubber molecules. However, no direct proof of such process in the vulcanization of rubber has been obtained. Hull and others (*RUBBER CHEM. & TECHNOL.* **20**, 649, 1947) and also Bloomfield (*RUBBER CHEM. & TECHNOL.* **21**, 543, 1948) carried out such reactions with model compounds of low molecular weight. We attempted with M. A. Vaskovskaya to follow the kinetics of thiol group formation

during the vulcanization of mixtures with and without zinc oxides. The vulcanizate was extracted with cold acetone and then ground in a mortar with granulated sugar to a fine state of subdivision. The sugar was leached out of the vulcanizate sample with water, the sample was dried, and covered with ligroin (to swell the particles) and with lead acetate solution. The reaction was continued for 25 hours with continuous shaking. The vulcanizate was then filtered off and successively washed with alcohol-ligroin mixture, pure alcohol, and finally pure water until lead ions were absent from the filtrate. After the washing, the filtrate was treated with an exact amount of 0.5 N sulfuric acid; the unreacted acid was titrated with NaOH solution with phenolphthalein indicator. The thiol group content was determined from the amount of sulfuric acid required to decompose the $R_1-S-Pb-S-R_2$ complex. For a number of reasons this method cannot be regarded as faultless for the accurate determination of thiol groups; it is, however, acceptable for a comparative evaluation of the thiol group content in the mixture at different stages of vulcanization.

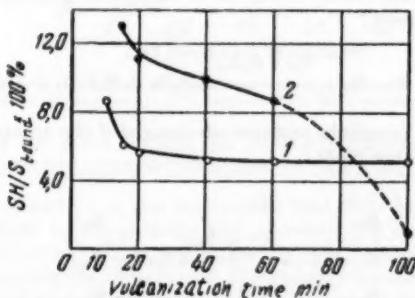
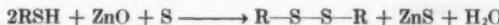
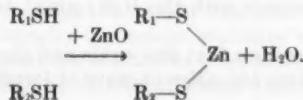


FIG. 9.—Variation of the thiol group content during vulcanization of sodium butadiene rubber; accelerator MBT: 1) mixture without ZnO; 2) mixture with ZnO.

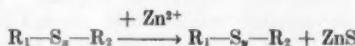
Figure 9 represents the variation of the thiol group content of mixtures with MBT, with and without ZnO. In the first case there is a decrease of the thiol group content during the first 20 minutes of vulcanization; subsequently the thiol group content is practically unchanged, and remains at a level of 6 per cent of the total amount of bound sulfur. In the second case, the initial thiol group content (after 10 minutes of vulcanization) is high, but this decreases gradually, and at the end of vulcanization it reaches a minimum value of ~ 2 per cent of the bound sulfur. These results indicate that during vulcanization thiol groups are oxidized with formation of crosslinks, and that zinc oxide participates in this process, probably by the mechanism proposed by Armstrong⁴



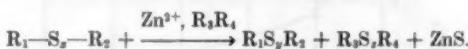
On the basis of model reactions, the crosslinkage effect may also be regarded as the consequence of the formation of zinc mercaptide:



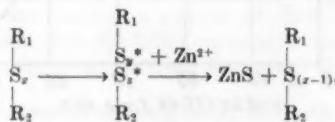
c) As was described earlier, it was shown in experiments with low-molecular polysulfides and with extracted vulcanizate containing polysulfide groups that zinc oxide and zinc salts react with polysulfides to form ZnS (Reactions 5, 6, and 7). The reaction with the polysulfide bonds in the vulcanizate structure evidently follows the scheme



and leads to the formation of crosslinks with fewer sulfur atoms¹¹. The number of crosslinks can either increase or remain unchanged. The case of a regrouping which leads to a decrease in the number of crosslinks has been examined by Dogadkin and Tarasova¹¹; it occurs in the stabilization of radicals as the result of the addition of low-molecular weight compounds and the formation of intramolecular rings. An increase in the number of crosslinks will occur when part of the polysulfide sulfur is liberated in the form of a new biradical S_x, which reacts with the double bonds (or α -methylene groups) of the molecular chains at another point:

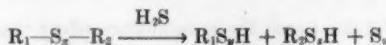


The number of crosslinks remains unchanged if the recombination of radicals occurs at the same point:



In the regrouping of polysulfide bonds without participation of zinc oxide or zinc compounds, there is a great probability of an increase in the number of crosslinks because the unlinked sulfur radicals are not wasted on the formation of zinc sulfide or polysulfide. This is confirmed by the data shown in Figure 7. The relative increase in the number of crosslinks which we observe after the sulfur is bound and which could be explained by regrouping of polysulfide bonds, appears to be greater in the mixtures which do not contain zinc oxide. (See the vertical branch of the curves which describe the change in the number of crosslinks with the amount of bound sulfur.)

The role that zinc oxide and zinc salts play in changes in the structure of vulcanizates is shown by the participation of these compounds in side reactions. It is known that H₂S is able to cause the decomposition of polysulfide bonds according to the equation:



The action of zinc compounds with the H₂S formed during vulcanization inhibits such a process.

The experimental data show that zinc oxide and zinc compounds take part in various reactions. There are different ways of forming ZnS during vulcan-

ization. Therefore, at the present time we can not accept the statement of Armstrong⁴ (that ZnS content can be employed as a measure of the quantity of disulfide bonds in the vulcanizate) because ZnS forms not only because of reactions with thiols, but also as a result of the other reactions described above. Furthermore, due to the above mentioned considerations, the number of cross-links in the vulcanizate is not a linear function of the zinc sulfide content as is proved by Figure 10.

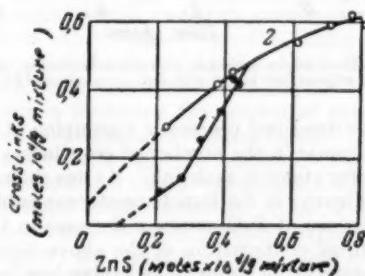


FIG. 10.—Variation of the number of crosslinks with the ZnS content in sodium butadiene rubber vulcanizates; 1) DPG accelerator; 2) MBT accelerator.

EFFECT OF ZINC OXIDE ON ISOTOPE EXCHANGE OF VULCANIZATES WITH ELEMENTARY SULFUR

In the previous section it was established that ZnO helps to increase the number of crosslinks in vulcanizates and decreases the degree of "sulfidity" (number of atoms of sulfur) in the links. It was interesting to prove this statement by analyzing the structure of vulcanizates by the method of isotope exchange which was worked out by Dogadkin, Tarasova and Kaplunov. For

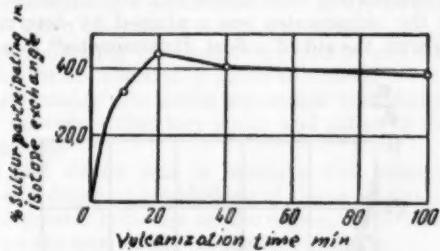


FIG. 11.—Isotope exchange of elementary sulfur with vulcanizates containing S³⁵.

this purpose the vulcanizate, which was obtained by using sulfur containing S³⁵, was extracted and was then heated with elementary nonradioactive sulfur at 130° C for three hours. The degree of exchange for different vulcanization times is shown in Figure 11. It is seen that the amount of exchange first increases, reaches a maximum at the time of optimum cure, and then gradually decreases. Since the capacity for isotope exchange with elementary sulfur is lower with decreasing quantities of sulfur in polysulfide bridges¹¹⁻¹³, the presence of the decreasing exchange curve after optimum cure appears to be direct con-

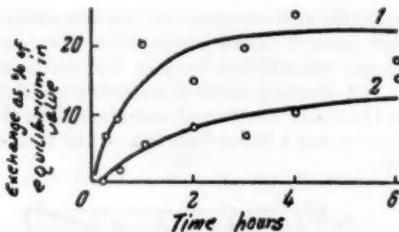


FIG. 12.—Kinetics of isotope exchange, with elementary sulfur, of vulcanizates:
1) without ZnO and 2) with ZnO; accelerator MBT.

firmation of the above described process of regrouping of polysulfide bonds in the direction of an increase in the number of crosslinks and a decrease in the average number of sulfur atoms in each link. As was shown by the experiments of Z. N. Tarasova (Figure 12) for butadiene-styrene rubbers, in all stages of vulcanization the presence of ZnO causes a decrease in the degree of isotope exchange, which is direct confirmation of the above demonstrated participation of ZnO in the formation of sulfur links having less "sulfidity".

EFFECT OF ZINC OXIDE ON THERMOMECHANICAL STABILITY OF VULCANIZATES

In the work of Dogadkin and Tarasova¹¹ it was shown that the character of vulcanizate structure influences the thermal and mechanical stability of vulcanizates and their behavior during aging and fatigue. It was therefore to be expected that vulcanization activators, by influencing the number and the nature of the vulcanization bonds, should also affect their heat stability. For confirmation of this, vulcanizates were prepared from mixtures compounded on microrollers mounted in a closet filled with pure nitrogen. Thus, both the mixing and the vulcanization were carried out with exclusion of oxygen. The heat stability of the vulcanizates was evaluated by determination of stress relaxation curves with the aid of a float dynamometer¹⁴ in a nitrogen atmos-

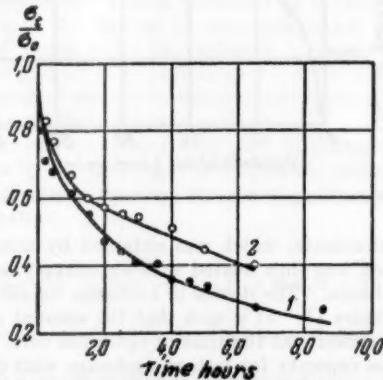


FIG. 13.—Stress relaxation of vulcanizates based on sodium butadiene rubber at 126°;
1) mixture without ZnO; 2) mixture with ZnO.

sphere at 126°. Figure 13 shows the relative stress relaxation in specimens stretched to 100 per cent; a vulcanizate containing MBT, zinc oxide, and stearic acid shows much slower relaxation, with a higher value of quasi-equilibrium stress, than a vulcanizate of the same composition without ZnO. Therefore, the vulcanizate containing ZnO has the greater heat stability. The rate constant of stress relaxation at 126° was, in the first case, $K_{126} = 1.38 \cdot 10^{-3}$ minute⁻¹, and in the second, $K_{126} = 2.52 \cdot 10^{-3}$ minute⁻¹. As stress relaxation in these conditions is due to cleavage and regrouping of chemical bonds¹¹, the results show that vulcanizates with zinc oxide contain more stable bonds of the type —C—C—, —C—S—C—, —C—S—S—C—, and a relatively lower content of polysulfide bonds of the type —C—S_z—C—. Thus, the experiments on stress relaxation are in good agreement with the above data on the effect of vulcanization activators in increasing the number of vulcanization bonds and decreasing the number of sulfur atoms in these bonds.

It is also important to note that the maximum swelling of vulcanizates without zinc oxide decreases, and that of vulcanizates with ZnO increases after relaxation. This difference in the behavior of the vulcanizates under the action of heat and mechanical stress is probably explained by the fact that, as was pointed out earlier, the cleavage of polysulfide linkages in absence of ZnO leads to the formation of new sulfur biradicals, which form additional new crosslinks. In the presence of zinc oxide and zinc compounds these radicals are "trapped" with the formation of zinc sulfide.

Thus, vulcanization activators have a significant influence not only on the formation of vulcanization structures at the time of vulcanization, but also on changes in them under the action of thermomechanical (and probably oxidative) influences in use.

SUMMARY

1. Zinc oxide and stearic acid do not affect the rate of addition of sulfur to rubber in the vulcanization of pure sodium butadiene rubber in mixtures without accelerators.
2. In mixtures containing diphenylguanidine as accelerator zinc oxide and stearic acid do not affect the rate of addition of sulfur to rubber.
3. In mixtures containing mercaptobenzothiazole zinc oxide retards and stearic acid accelerates the addition of sulfur to rubber.
4. In a similar manner zinc oxide suppresses and stearic acid activates isotope exchange between elementary sulfur and sulfur of the thiol group in mercaptobenzothiazole.
5. Zinc oxide and stearic acid in mixtures with mercaptobenzothiazole increase the rate and degree of crosslinking of the molecular chains of rubber; zinc oxide has the greater influence on the degree, while stearic acid has the greater influence on the rate, of the crosslinking reaction.
6. In mixtures with diphenylguanidine the influence of vulcanization activators on the degree and rate of crosslinking is considerably less pronounced than in mixtures with mercaptobenzothiazole.
7. The kinetics of zinc sulfide formation during vulcanization has been studied and it was established that ZnS is formed as the result of reactions of zinc oxide and zinc compounds with thiol and polysulfide groups in the rubber. Model substances have been used to demonstrate other possible routes for the formation of zinc sulfide during vulcanization. The effect of zinc oxide and stearic acid on the rate and degree of crosslinking is associated with participation of these compounds in such reactions.

8. Isotope exchange between radioactive sulfur in the vulcanizate and elementary sulfur was used to follow the formation and changes in the numbers of polysulfide linkages during the vulcanization process. The amount of sulfur participating in isotope exchange as vulcanization proceeds at first increases, passes through a maximum, and then decreases, which indicates a regrouping of the polysulfide linkages with an increase in their number and a decrease of the average number of sulfur atoms per linkage. Zinc oxide decreases the degree of isotope exchange between the vulcanizate and elementary sulfur at all stages of vulcanization.

9. Vulcanization activators, by favoring a decrease in the number of sulfur atoms in the sulfur bonds, increase the heat stability of the vulcanizates. This effect of the activators was demonstrated by kinetic data on stress relaxation in deformed vulcanizates at 126°.

10. The cleavage and regrouping of polysulfide linkages in the presence of zinc oxide and zinc compounds is accompanied by the combination of part of the sulfur as zinc sulfide, which leads to a decrease in the number of newly formed crosslinks. This effect of zinc oxide is manifested in vulcanization reversion effects and in changes of vulcanizate properties under thermomechanical influences.

11. From the above experimental data the general conclusion may be drawn that the fundamental role of vulcanization activators does not lie in their influence on the kinetics of the addition of sulfur to rubber, but rather in their influence on the nature of the vulcanization structures formed and on changes in them in the course of vulcanization.

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THE MECHANISM OF ACCELERATOR ACTION. REACTION OF MERCAPTOBENZOTHIAZOLE WITH SULFUR *

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The investigation of the reaction of sulfur with mercaptobenzothiazole (MBT) is of great interest from the point of view of clarifying the mechanism of the action of the latter as a vulcanization accelerator. We studied the reaction of MBT with elemental sulfur in the melt and in solvent media—vaseline oil and xylene. The course of the reaction was followed by means of the H₂S liberated, which was removed from the reaction medium by a continuous stream of nitrogen and was absorbed in a solution of CdCl₂.

In Figure 1 are presented the kinetics of the liberation of H₂S on heating the mixture in a medium of vaseline oil, the concentration of MBT and sulfur comprising, respectively, 0.06 mole/liter and 0.655 g-atom/liter. This ratio and concentration of reactants corresponds to those in the vulcanization of rubber. As can be seen, the splitting out of H₂S under the stated conditions proceeds at a constant rate, which can be explained by the very insignificant change in concentrations of reactants over the entire time (only 1.5% of the MBT introduced reacted in 10 hours at 140°). The kinetics of the liberation of H₂S from a melt of MBT and sulfur at 140° practically coincide with the kinetics of the reaction in solution (see Figure 1). The temperature dependence of the rate constants leads to the expression $K = 3.54 \cdot 10^{10} e^{33600/RT}$.

The reaction proceeds analogously in a xylene medium at the boiling point ($\approx 138^\circ$). The only difference consisted of some excess of liberated H₂S in comparison with the reacting MBT. Meanwhile, control experiments showed that, under the stated conditions, neither sulfur nor MBT separately reacted with xylene. Splitting of hydrogen from a molecule of the latter occurred only on the joint action of sulfur and MBT, that is, as a result of reaction with those intermediate compounds (free radicals) formed by the interaction of sulfur and MBT.

In Figure 2 are presented data characterizing the change in the rate v , of the liberation of H₂S with a change in the concentration of reactants. From these data it is seen that the reaction rate increased linearly with an increase in the total concentration of sulfur and MBT. However the ratio v/C , where C is concentration, increased with an increase in the concentration of MBT (see Table I) and decreased with an increase in the concentration of sulfur. The latter phenomenon can be explained by the absorption by the sulfur, under the conditions of the reaction, of SH radicals forming compounds¹ of the type HS—S_x—SH. With an increase in the concentration of sulfur (above a certain limit), there is an increase in the amount of SH groups.

* Reprinted from the *Proceedings of the Academy of Sciences USSR*, Chemistry Section, Vol. 108, pages 237-240 (1950), an English translation of Consultants Bureau, Inc.; *Doklady Akad. Nauk SSSR* 108, 259-262 (1956).

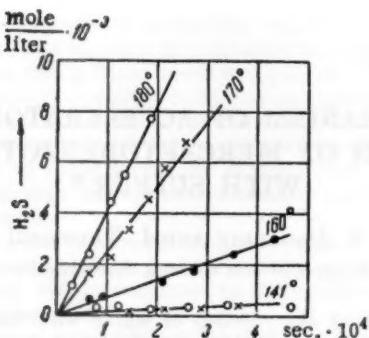
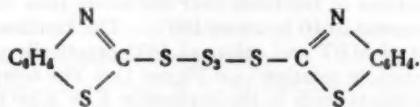


FIG. 1.—Kinetics of the liberation of H_2S on heating sulfur and MBT at various temperatures in a vaseline oil medium.

The kinetics of the liberation of H_2S are greatly accelerated by the introduction of stearic acid (an activator for the vulcanization process) into the reaction mixture, and they are completely suppressed by oxides of nitrogen. The latter fact can be considered as indirect evidence of the radical mechanism of the interaction of sulfur and MBT.

As a result of the reaction, MBT is converted into a polysulfide of the elemental composition: C, 37.94%; S, 52.5%; N, 6.05%; and H, 2.69%, which corresponds to the average formula



M. p. (with decomposition) $\approx 130^\circ$. The absorption spectrum of the polysulfide (see Figure 3) has a maximum in the region of $330 \text{ m}\mu$, which is characteristic of linear polysulfides². Since the polysulfides undergo dispro-

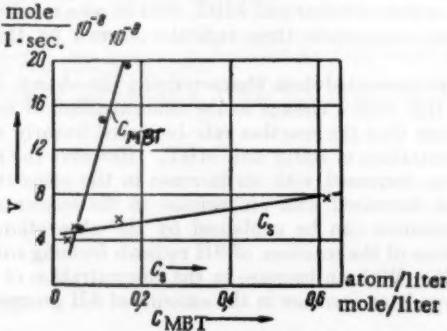


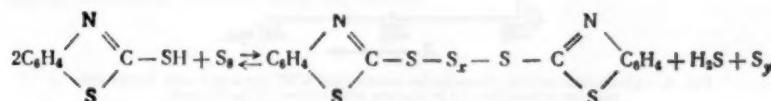
FIG. 2.—Dependence of the rate of H_2S liberation on the concentration of sulfur (C_s) and MBT (C_{MBT}).

TABLE I

MBT concentration, in moles/liter	S concentration, in g-atoms/liter	Rate constant, sec ⁻¹ .10 ³
0.06	0.0318	13.4
	0.0655	7.5
	0.157	4.0
	0.627	1.01
0.0595		8.3
0.119	0.0655	13.0
0.179		11.3

portionation at a temperature of 140° , the cited analytical data, obviously, characterize the average composition of polysulfides with a variable number of sulfur atoms in the polysulfide bridge.

The formation of hydrogen sulfide was not observed on heating sulfur and MBT in sealed ampoules at 140° . From this it follows that the equilibrium of the reaction, in conformity with the equation:



is characterized by an insignificant concentration of H_2S and appreciable liberation of hydrogen sulfide occurs only under the above-cited conditions of its continuous elimination from the sphere of the reaction.

In sealed ampoules, the reaction between sulfur and MBT in the melt leads: a) to an exchange of sulfur in the mercapto group⁴; b) to the formation of a polysulfide containing more than 42.9% sulfur. This polysulfide was extracted from the cold reaction mixture with an aqueous solution of NaOH, which indicates the presence in the polysulfide of a mercapto group. The spectrum of this substance contained a maximum in the region of $330 \text{ m}\mu$; however, it was not very clearly defined (see Figure 4). The polysulfide

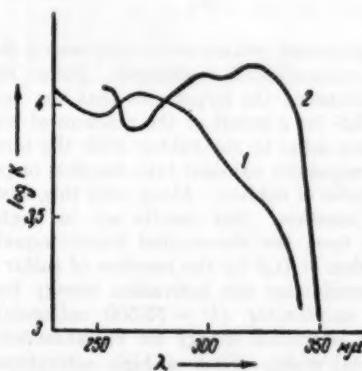


FIG. 3.—Absorption spectra of dibenzothiasolyl disulfide (1) and conversion products of MBT (2).

extracted with a solution of NaOH actually contained unchanged MBT; since the separation of these substances was not possible, the sulfur content presented above refers to the composition of the mixture. The sulfur content of the polysulfide itself is, obviously, substantially greater. The absence of free sulfur in the preparation was checked by the reaction of Garcia-Fernandez⁵.

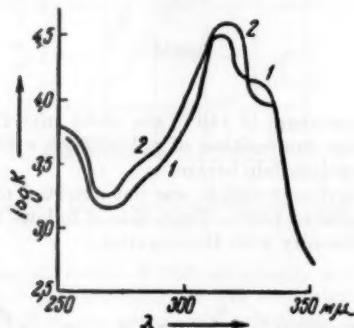
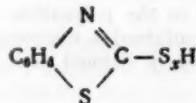


FIG. 4.—Absorption spectra of conversion products of MBT extracted with NaOH after reaction with sulfur: 1) in mixture with rubber; 2) in the melt.

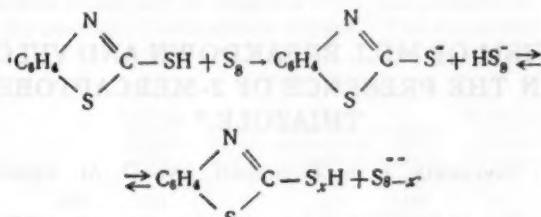
An analogous substance was extracted from a mixture of natural rubber, sulfur, and MBT after vulcanization in a press. The sulfur content of this polysulfide was more than 50.2%; the maximum in the region of 330 mμ was rather clearly evident.

Thus, the intermediate compound formed by the reaction of sulfur and MBT under vulcanization conditions is a polysulfide of the composition

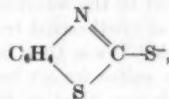


The experimental data permit certain considerations on the mechanism of the action of MBT as a vulcanization accelerator. Fisher and a series of other investigators⁶ have advanced the hypothesis that the vulcanization reaction is the formation of H₂S (as a result of the reaction of sulfur with rubber or accelerator) which then adds to the rubber with the formation of mercapto groups which are subsequently oxidized into disulfide or polysulfide "bridges" between molecular chains of rubber. Along with this, Fisher assumes a chain mechanism for this reaction. Our results are in contradiction with this hypothesis. As seen from the above-cited kinetic equation, the activation energy for the formation of H₂S by the reaction of sulfur and MBT is 33,500 cal/mole, which approximates the activation energy for the vulcanization process without an accelerator ($U = 35,500$ cal/mole) and considerably exceeds the apparent activation energy for vulcanization in the presence of MBT ($U = 20,900$ cal/mole). Such a high activation energy means an extremely slow process, and, therefore, the formation of H₂S cannot be considered as basic to vulcanization.

The following scheme for the reaction of sulfur with MBT under vulcanization conditions seems more probable to us:



This scheme is confirmed by the discovery of a polysulfide of MBT in the reaction system. The formation of polysulfide as an intermediate product during the reaction of MBT with sulfur was assumed in a previous work⁷. The vulcanization effect is basically determined by the reaction of rubber with sulfur biradicals, S_{8-x}^{\cdot} and with the radical



the action of which under vulcanization conditions has been considered by us previously⁸.

ACKNOWLEDGMENT

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MECHANISM OF MILL BREAKDOWN AND VULCANIZATION IN THE PRESENCE OF 2-MERCAPTOBENZOTHIAZOLE *

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The mechanism of the action of 2-mercaptopbenzothiazole, MBT, one of the most commonly employed accelerators of vulcanization, remains unclear. L. Wistinghausen¹ and B. A. Dogadkin and D. M. Pevzner (1951, unpublished) showed that MBT is consumed in vulcanization, but these authors, because of the crudity of their methods, did not obtain quantitative relationships.

In the present work there has been employed a preparation of the MBT which was tagged in the thiazole ring by the radioisotope S³⁵. The synthesis² of this compound was carried out in the following manner. MBT, tagged in both of its sulfur atoms, was first synthesized from phenyl isothiocyanate and elementary S³⁵. The resulting MBT was then heated in a sealed ampule with an excess of inactive elementary sulfur for six hours at a temperature of 140°. Under these conditions the exchange reaction between the elementary sulfur and the sulfur of the mercapto group of the MBT reaches equilibrium³. The activity of the resulting MBT fell to one-half of the original value. In this way the benzothiazole radical was tagged, by the introduction into the molecule of MBT of the radio-isotope S³⁵ which does not exchange with elementary sulfur, under the conditions of vulcanization, and it thus became possible to measure simultaneously the velocity of the addition of the sulfur and the velocity of addition of the accelerator to the rubber.

Vulcanization was investigated in a mixture containing natural rubber (NR) which had been extracted from a benzene solution and dried, and also, in a mixture containing a sodium-butadiene rubber (SKB). The compositions of the mixtures are indicated in Table I. The combined sulfur (the elementary sulfur and also that which enters into the structure of the accelerator) was determined in the vulcanizate, after extraction with acetone, by means of oxidation with a mixture of HNO₃ and Br₂ in the presence of MgO⁴. The MBT which was combined with the rubber was determined by a radiometric method⁵. From the maxima of the swelling of the vulcanizate in acid solution there was calculated the number of crosslinkages, using the equation of Flory and Rehner⁶.

In Figure 1 data are given concerning the kinetics of the addition of sulfur and MBT during the process of vulcanization of NR at 121°. The reaction of addition of the sulfur to the rubber and that of addition of the accelerator proceed in a similar fashion. In the presence of the activator ZnO there is observed a more intensive combination of the accelerator, whereas this activator does not influence the velocity of the combination of the sulfur.

A small quantity of the MBT combines with the rubber even on the mill during the preparation of the mixture. In order to interpret the mechanism

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of this combination of the MBT during milling, natural rubber, was purified by a 20 hour extraction with cold acetone in an atmosphere of pure nitrogen, with an addition of one part by weight of MBT was subjected to a 20 minute milling in the absence of atmospheric oxygen. The masticated rubber was

TABLE I

Composition of mixture		Temperature of vulcanization, °C	Time of vulcanization, min	Combined elementary S (g-atoms/g) · 10 ⁴	Combined MBT (moles/g) · 10 ⁴	Number of cross linkages (moles/g) · 10 ³	Number of molecules of MBT reacted per cross linkage
NR	100	121	0	—	1.00	—	—
S	4		20	3.52	2.84	6.27	0.29
MBT	2		40	5.10	3.16	8.97	0.24
			60	5.65	3.72	10.80	0.25
PBNA	1		80	6.22	4.11	10.26	0.30
ZnO	5		100	7.16	4.12	10.88	0.28
Stearic acid	2		120	8.38	4.22	14.0	0.23
SKB	100	140	0	—	0.37	—	—
S	2		5	3.88	0.47	0.45	0.20
MBT	1		10	5.04	0.56	0.91	0.20
PBNA	1		20	5.97	0.92	1.20	0.45
			30	5.95	1.38	1.60	0.63
			40	5.95	1.36	1.66	0.59
			60	6.11	1.66	2.19	0.58

then separated into fractions in a binary benzene-methyl alcohol solvent by the reduction of the temperature. The viscosity was determined for each fraction in benzene solution and the quantity of the combined MBT was evaluated by a radiometric method. It is to be seen from Table II that the amount of the combined MBT increases, up to a certain point, with the

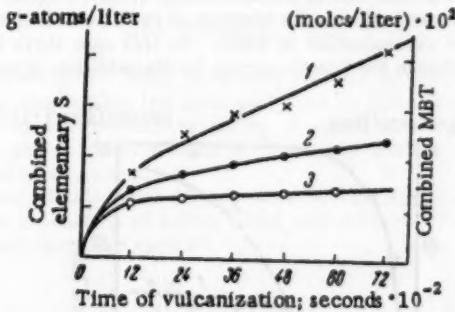


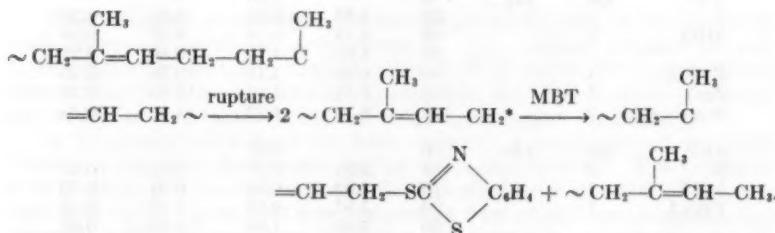
Fig. 1.—The kinetics of the addition of sulfur (1) and MBT during the vulcanization of natural rubber in a mixture with ZnO (2) and without ZnO (3).

increase of the order number of the fraction; that is to say, with a decrease of the molecular weight. Such behavior can be explained by the fact that the MBT adds to the polymer radicals which are formed during mechanical rupture. The rupture of the molecular chain of rubber occurs, in all likelihood, at a bond which unites allyl groups, since this bond is weakened by the effect of conjugation to approximately 45 kcal/mole. The radicals which thus arise

TABLE II

Number of fraction	I/I_0	Amount of combined MBT (moles/liter) $\cdot 10^3$	[%]
Unfractionated	—	—	—
1	0.053	3.21	12.0
2	0.091	5.45	24.5
3	0.110	6.22	9.2
4	0.071	4.28	8.0
5	0.090	5.30	5.5

interact with the molecules of the MBT according to the scheme:



As a result the content of MBT in the low molecular fraction is considerably greater than it is in the high molecular fraction. If the MBT reacted at the double bonds there would not be observed this distribution of it among the fractions of the masticated rubber. In the presented scheme the MBT reacts in the thiol form; the interaction in the thione form leads to exactly the same results for the distribution among the fractions.

The MBT which unites with rubber during milling also accelerates the process of vulcanization, but to a considerably smaller degree.

In Figure 2 there is shown the kinetics of the addition of sulfur and MBT in the process of vulcanization of SKB. In this case there is also observed the similarity between the kinetic curves for the addition of sulfur and for the

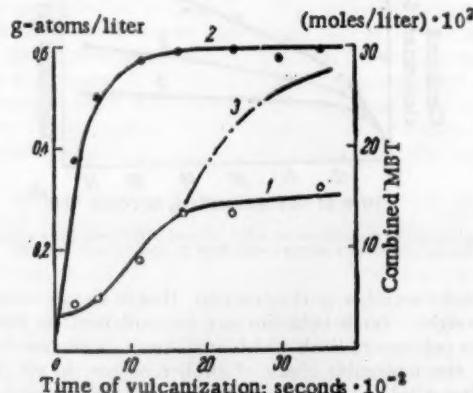


FIG. 2.—The kinetics of the addition of MBT (1) and sulfur (2) during vulcanization; (3) after the introduction of 2% sulfur by diffusion from solution.

addition of MBT. At the moment of the complete union of the sulfur (30 minutes) the velocity of the addition of the MBT sharply diminishes, although the concentration of the latter in the mixture is still rather high. This fact indicates that the reaction of MBT with the rubber proceeds with appreciable velocity only in the presence of sulfur, a fact which agrees with the data concerning the catalytic action of sulfur on the addition of mercaptans to olefins⁷. Actually, our experiments have shown that a subsequent addition of the sulfur into the vulcanizate during its swelling (in the stage of the depletion of the free sulfur) leads, once more, to an acceleration of the reaction of addition of MBT to the rubber (Figures 2, 3).

The kinetics of the addition of sulfur to rubber, in the presence of MBT, is satisfactorily described as a reaction of first order in sulfur. The velocity constants calculated according to such an equation vary linearly with the concentration of MBT (Figure 3). The energy of activation for the vulcanization SKB under the customary ratio of sulfur to accelerator proves equal to 20.6 kcal/mole.

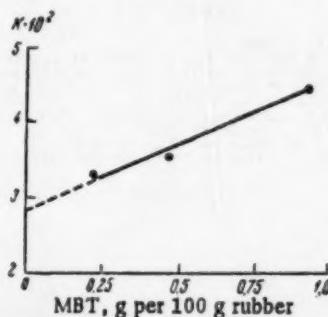
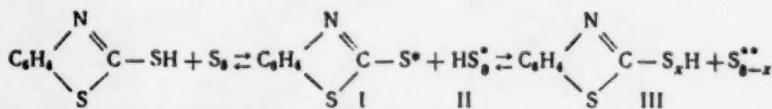


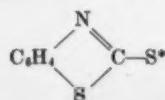
FIG. 3.—The relationship between the velocity constant for the addition of sulfur and the concentration of MBT.

The ratio between the MBT consumed and the number of crosslinkages (see Table I) is considerably less than unity and in the principal phase of the vulcanization this ratio remains constant. A calculation shows that per one combination of the accelerator there occurs approximately two instances of the formation of crosslinkages.

The experimental data which are presented here indicate the interdependent character of the interaction of sulfur, MBT and rubber. This action clearly follows the scheme proposed earlier⁸:



Under the conditions of vulcanization the radical



either interacts with the α -methylene groups of the molecular chains of the rubber (reducing to MBT) or adds at a point where there is a double bond. In either case there are formed polymeric radicals which are capable of interaction, either between themselves or with reactive low molecular groups. The radical HS_n^* unites with a molecule of rubber forming polymeric mercaptans; oxidation of the latter, or their interaction at double bonds, leads to the production of polysulfide bonds between the rubber chains. The recombination of the radicals I, II results in the formation of 2-benzothiazolyl-hydriopolysulfide (III), which in turn separates out a variable number of atoms of sulfur in the form of biradicals, which latter directly unite the molecular chains of the rubber at the positions of double bonds.

In the complicated sequence of the reactions of vulcanization the initial process is the interaction of the MBT and the sulfur. For this reason the speed of the combination of the sulfur and the rubber, as has already been pointed out, is found to depend linearly on the concentration of the MBT.

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ROLE OF HYDROGEN DISULFIDE IN VULCANIZATION *

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In a previous investigation¹ we have shown that many vulcanization accelerators, including ethylenediamine and its derivatives, ethanolamines, and hydroxy carbonyl compounds, react with sulfur at the vulcanization temperature with formation of hydrogen sulfide as main product. By analogy to many oxidation-reduction systems in which oxygen takes part and reacts through hydrogen peroxide formation, the reaction of sulfur with vulcanization accelerators can be regarded as follows in which DH₂ is the vulcanization accelerator.



The species responsible for the initiation of the vulcanization process are SH radicals formed by the breakdown of hydrogen disulfide or hydrogen polysulfide. The breakdown of hydrogen disulfide in rubber solution at 50–70° results in the transformation of the rubber into a gel¹. Its breakdown in paraffins and aromatic hydrocarbons leads to quantitative separation of hydrogen sulfide and sulfur^{1,2}. We have shown that in the breakdown of hydrogen disulfide in α-olefins (styrene, α-methylstyrene, 1-pentene, and isoprene), which act as acceptors for free radicals, reaction proceeds at 50–70° without formation of hydrogen sulfide and sulfur, but with formation of addition products (mono-, di-, and tetra-sulfides).

The suppression of the reaction leading to evolution of hydrogen sulfide is associated with trapping of the intermediate breakdown product (the ·SH radical) by unsaturated compounds. Similar effects are observed when sulfur reacts with monoethanolamine in 1-pentene or α-methylstyrene solution at 130°. In ethylbenzene solution this reaction leads to the evolution of 80% of the theoretical amount of hydrogen sulfide. In the α-olefins, only addition occurs without formation of hydrogen sulfide. Table I gives the compositions of products obtained by reaction of hydrogen disulfide with 1-pentene and of sulfur with monoethanolamine in presence of 1-pentene.

The formation of mono- and polysulfides is associated only with the formation of active intermediate products of the breakdown of hydrogen disulfide, for hydrogen sulfide does not add to the double bond in absence of free radicals. The formation of the products indicated can be explained on the assumption

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TABLE I
COMPOSITIONS OF THE PRODUCTS^a OF THE REACTION OF 1-PENTENE WITH HYDROGEN DISULFIDE
AND WITH SULFUR AND MONOETHANOLAMINE

Fraction	Identity of fraction	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Molecular weight	Elementary composition, %			Yield of fraction, %
						C	H	S	
Hydrogen disulfide + 1-pentene: 15 hours, 50° concentration of H ₂ S ₂ in pentene: 0.925 mole/liter									
I	Pentyl sulfide	86-87 (12-13)	0.8446 (0.8439)	1.4572 (1.4584)	174 (174)	68.44 (68.96)	12.72 (12.64)	18.37 (18.39)	62
II	Pentyl disulfide	68-75 (1)	0.9381		201 (206)	58.2 (58.25)	10.58 (10.68)	30.44 (31.07)	12.1
III		76-96 (1)				56.28	10.48	33.84	
IV	Pentyl tetrathulfide	100-107 (1)	d_4^{20} 1.0134	n_D^{20} 1.5280	268 (270)	47.25 (44.44)	8.92 (8.15)	43.84 (47.50)	22.0
Sulfur + monoethanolamine + 1-pentene: 10 hours, 130°; concentration of S: 0.89 mole/liter; concentration of monoethanolamine: 1.0 mole/liter;									
I	Pentyl sulfide	86-90 (12)	0.8437	n_D^{20} 1.4568	170	68.66	11.54	19.47	28.6
II	Pentyl disulfide	120-125 (12-13)	0.9310	n_D^{20} 1.5001	208	62.17	9.97	27.95	30.0

^a Data from literature and calculated molecular weights and compositions are given in parentheses.

that HS^- and HS_2^- radicals take part in the initiation and development of the process.

EXPERIMENTAL

Hydrogen disulfide, b.p. 75° , was prepared by fractional distillation of hydrogen polysulfide³. 1-Pentene was prepared from ethyl bromide and allyl chloride⁴; it had b.p. 30° , n_D^{20} 1.3720; and d_4^{20} 0.6589. Isoprene, styrene, and α -methylstyrene were freed from stabilizer by shaking them with sodium hydroxide solution, after which they were washed with water, dried, and distilled.

The reactions were carried out in sealed tubes in a nitrogen atmosphere. At the end of the period of heating the tubes were cooled to -78° and H_2S was removed. The completeness of the decomposition of H_2S was determined by shaking with CdCl_2 solution: absence of a precipitate of CdS_2 indicated complete decomposition of H_2S_2 . In the solution, after treatment in this way, the mercaptan content and the total amount of elementary and polysulfide sulfur were determined⁵. 1-Pentene was distilled off and the residue was vacuum fractionated.

SUMMARY

It was shown that the breakdown of hydrogen disulfide in α -olefins results in the exclusive formation of addition products (mono-, di-, and tetrasulfides) without formation of hydrogen sulfide and free sulfur. Similar results were obtained when sulfur reacted with monoethanolamine (vulcanization accelerator) in α -olefin solution.

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THE RADIOACTIVE TRACING OF THE DIFFUSION OF SULFUR IN CABLE RUBBERS *

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The use of radioactive isotopes is a progressive and promising innovation in the study of the manufacture of cable rubber¹. Thus, in an earlier article the authors demonstrated the possibility of using the radioactive isotope of sulfur, S³⁵, in the study of diffusion processes in cable rubbers during vulcanization. The use of labelled sulfur as the vulcanizing agent in core rubber mixtures has shown:

(1) an intensive diffusion of sulfur from the core rubber mixture into the insulating rubber during vulcanization;

(2) the presence of a high concentration of accelerators in a thin (0.1 mm) surface layer of the insulating rubber; this is a fundamental cause of the overcure of the insulating rubber, which leads to the appearance of cracks, accelerated aging, and other defects;

(3) an intensive exchange of sulfur atoms among the accelerators and between them and the bound polysulfide sulfur.

Thus, as a result of the diffusion of sulfur from the core mixture to the insulating rubber, the nature of the sulfur bonds is changed, and a number of polysulfide structures are formed. It has been shown² that the polysulfide-bound sulfur is mobile, that is, it takes part not only in the isotopic exchange of sulfur atoms, but also in the diffusion process. According to Bresler³, the coefficients of diffusion of free polysulfide sulfur can be calculated from measurements of the radioactivity.

Diffusion of free sulfur.—The coefficient of diffusion of free sulfur at high temperatures can be determined by the empirical formula:

$$I_{(t_1 d)} = I - 2Ie^{-(\pi/d)^2 D t} \quad (1)$$

where $I_{(t_1 d)}$ is the radioactivity measured by a counter on the surface, d , I is the radioactivity measured on the surface after the concentrations are equalized, and t is the time.

In order to study the diffusion of free sulfur at lower temperatures, where diffusion proceeds slowly, another empirical formula is more adaptable:

$$I_{(t_1 d)} = \frac{I_0}{\sqrt{\pi D t}} e^{-d^2/4 D t} \quad (2)$$

Plotting the value $1/t$ on the abscissa and $\log I t$ on the ordinate, we obtain a curve, the tangent of the angle of slope of which determines the coefficient of diffusion. The absolute values of the coefficient of diffusion, calculated for

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specimens of various thickness by various formulas, are the same, i.e., of the order of 10^{-6} sq cm/sec at 130–150° C, a value which is typical of the diffusion of small molecules in a viscous liquid. The coefficient of diffusion of sulfur in natural rubber at various temperatures is described quantitatively by the formula:

$$D = D_0 e^{-Q/RT} = 0.0107 e^{-700/RT} \text{ sq cm/sec} \quad (3)$$

and is practically independent of the concentration of sulfur up to concentrations of 10 per cent. The coefficient of diffusion of sulfur is lower in vulcanized rubber than in crude rubber, and is expressed by the formula:

$$D = 0.0060 e^{-700/RT} \text{ sq cm/sec} \quad (4)$$

The coefficient of diffusion of sulfur in sodium-butadiene rubber (SKB) is described by the formula:

$$D = 2.91 e^{-15,000/RT} \text{ sq cm/sec} \quad (5)$$

It was established from measurements of radioactivity that the coefficient of diffusion of the vulcanizing agent of the insulating rubber, which was tetramethylthiuram disulfide (thiuram), at 115° C was 0.74×10^{-6} sq cm/sec and at 125° C was 1.3×10^{-6} sq cm/sec; that is, the molecules of free thiuram diffuse at roughly the same rate as those of free sulfur.

Diffusion of polysulfide (bound) sulfur.—The mobility of polysulfide bound sulfur is a result of the chemical dissociation of the polysulfide chains and their absorption at other points. The coefficient of this chemical diffusion is much lower than that of free dissolved sulfur. It was found that the quantity of sulfur diffused from radioactive rubber into the adjacent upper layer (the diffusion recipient) was considerable when this layer was vulcanized rubber. If migration takes place from the vulcanizate into the crude rubber, then it appears that only a slight amount of sulfur passes into the crude rubber.

It was also found that the degree of dissociation, β , of migrating polysulfur at 160° C was 22 per cent. The empirical formula for the study of the migration of polysulfide sulfur by means of radioactive isotopes can be expressed by the equations:

$$\frac{I}{I_0} = kF(z); \quad z = \frac{\delta}{2\sqrt{D't}}; \quad k = \frac{C_0}{C_n}; \quad (6)$$

where C_0 is the initial concentration of sulfur capable of dissociation in vulcanized rubber; C_n is the total concentration of sulfur in the specimen after elimination of free non-reacting sulfur from the rubber by extraction; δ is the thickness; D' is the coefficient of diffusion of polysulfide sulfur, equal to D ; $F(z)$ is the calculated function, depending on the coefficient of absorption of the beta particles, of the radioactive sulfur in the rubber, SKN

$$\frac{I}{I_0} = e^{-\mu z}.$$

From these data the coefficient of chemical diffusion of sulfur D' in vulcanized natural rubber sheets 0.244 mm thick at 140.5° C was found to be 1.7×10^{-7} sq cm/sec. For sodium-butadiene rubber sheets 0.241 mm thick

the coefficient of chemical diffusion of sulfur at 151° C was 1.1×10^{-7} sq cm/sec. It is evident that in the vulcanization of various insulated cable rubber products with vulcanized casing, diffusion of both free sulfur and polysulfide sulfur takes place.

EXPERIMENTAL PART

It is of great practical importance to know whether cured rubber insulation can be protected from the degrading effect of diffusible sulfur. Diffusion of sulfur becomes of particular importance during the continuous curing of cables, when, in contrast with ordinary curing, the use of insulation rubbers with low-sulfur content is common practice.

The present study deals with the diffusion during vulcanization of sulfur from a core mixture into the insulation rubber, the two rubbers being separated by a thin layer of various materials⁴. The following materials were used: telephone paper, cable paper, metal-coated paper, rubber coated and plain sheeting; high-molecular thermoplastics, polyethylene, polyvinyl chloride, and polystyrene.

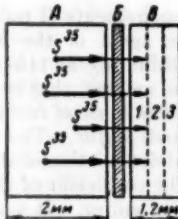


FIG. 1.—Position of samples in experiment for study of diffusion of sulfur from core compound, A, (letters at top of figure) through protective layer, B, into three-layer insulation, V.

The experimental method was as follows. One per cent of radioactive sulfur³⁵ was added to the core rubber mixture, and specimens 2 mm thick were sheeted out on a mill. The films of core rubber mixture containing S³⁵ were put together with a sheet of the material which served as the protective layer against diffusion of sulfur. The insulation rubber in the form of three sheets 0.3–0.4 mm thick was attached to the protective layer, so that the total thickness of the insulation rubber was 1–1.2 mm (see Figure 1). Each layer was dusted with talc in order to prevent vulcanization of one layer to the next one and to facilitate their separation after vulcanization. The specimens were vulcanized in a steam vulcanizer under industrial conditions at 145° C for 20, 40, and 60 minutes. After vulcanization, specimens of 16 mm diameter were cut out of each layer and their radioactivity was measured.

It is quite evident that radioactivity can develop in any layer only at the expense of the diffusion of sulfur from the core rubber, the surface content of which is directly proportional to the intensity of radiation (impulses per minute). The results of measurements of radioactivity in the insulating rubber are shown in Table I.

On the basis of the data in Table I it is possible to draw the following fundamental conclusions:

1. Neither rubber-coated nor plain sheeting serves as a barrier to the sulfur diffused by the core layer into the insulation rubber.

2. The highpolymer thermoplastics, i.e., polyethylene, polyvinyl chloride, and polystyrene do not serve as a barrier to sulfur diffusion.

3. Paper of the telephone, cable, and metal-coated types almost completely inhibits sulfur diffusion, that is, it is a true barrier against migrating sulfur.

In this connection the question arises of the practicability of the further use of uncoated sheeting in the manufacture of some cables. Would it not be more expedient and economical to omit uncoated sheeting from certain kinds of cables, or to use for this purpose one of the papers used as insulation in other cables? Of course it must be remembered that in the manufacture of cables,

TABLE I
RADIOACTIVITY OF INSULATION RUBBER AFTER VULCANIZATION

Barrier material ^a	Vulcanization time at 145° C, min	Core rubber	Barrier	Number ^b of impulses in 3 minutes		
				First layer	Second layer	Third layer
Talc	20	4268	—	3857/219	83/12	15/6
Polyvinylidene chloride	20	3838	552/483	3373/110	42/27	*
Polyethylene	20	2522	1104/524	1300/99	18/18	*
Polystyrene	20	4690	—	4329/90	20/4	*
Cable paper	20	4350	31/10	15/7	*	*
Telephone paper	20	4152	24/22	*	*	*
Metal-coated paper	20	3229	*	*	*	*
Talc	40	4311	—	4146/129	49/2	*
Polyethylene	40	4290	146/154	4060/85	27/4	*
Uncoated sheeting	40	3471	41/8	1084/114	*	*
Cable paper	40	4443	19/11	11/2	*	*
Telephone paper	40	4592	14/16	19/12	*	*
Metal-coated paper	40	2363	*	*	*	*
Polyvinyl chloride	60	2551	—	906/27	*	*
Polyethylene	60	4914	95/76	3991/60	*	*
Rubber-coated sheeting	60	4764	749/204	1838/63	26/15	12/9
Uncoated sheeting	60	2834	37/16	1242/24	*	*
Cable paper	60	4265	*	*	*	*
Telephone paper	60	4228	14/4	*	*	*

* Background (background count of Geiger counter).

^b Numerator: activity of contact surface; denominator: activity of opposite surface. Thickness of each layer of insulation rubber 0.35–0.40 mm.

^a Thickness of polyethylene 0.28 mm, polyvinylchloride 0.24 mm, rubber-coated sheeting 0.31 mm, telephone paper 0.05 mm, cable paper 0.12 mm.

sheeting serves as a wrapper during cure of the insulated coarse strands. It is quite possible that paper treated with synthetic polymers would also possess satisfactory physical and mechanical properties.

As has already been observed, low-sulfur insulation rubbers containing less than 0.3 per cent of sulfur, not including that in thiuram, are prescribed for the continuous vulcanization of cables. It is interesting to study the diffusion of this sulfur from the insulation into the copper of the conducting strands in the core rubber. For this purpose, isotopic sulfur³⁵ was added to the recipe of the insulation rubber mixture instead of ordinary sulfur. After preliminary undercure, the rubber was plied up with a thin (0.45 mm) sheet of copper on one side, and the core rubber on the other.

The results of measurements of the radioactivity of the materials after vulcanization are shown in Table II.

The data in Table II indicate first of all that the sulfur of the insulating

rubber is extensively diffused into the copper of the conducting strands, reacting chemically with the latter, and causing sulfurization (formation of copper sulfide). Treatment of the specimens of copper sulfide in acetone for 24 hours in order to eliminate free sulfur did not change the radioactivity of the specimens, indicating the presence of a chemical bond between the sulfur and copper. At the same time, diffusion of sulfur from the core to the insulation and vice versa also took place.

It is particularly important to note that labile, easily ruptured sulfur bonds are formed in rubbers containing sulfur, regardless of the nature of the accelerator. The number of mobile sulfur bonds depends on the nature of the accelerator, it is smaller in the case of thiuram and sulfur than in the case of such accelerators as mercaptobenzothiazole and diphenylguanidine. The sulfur structures of vulcanized butadiene-styrene rubber (SKS) contained fewer

TABLE II
RADIOACTIVITY OF MATERIALS AFTER VULCANIZATION FOR 35 MINUTES

Materials (in order of assembly)	Radioactivity in impulses every 3 minutes ¹
1. a) Copper sheet 0.45 mm thick	237/64
b) Insulating rubber 1.2 mm thick with radioactive isotope S ³⁵	413
c) Copper sheet 0.45 mm thick	91/56
2. a) Copper sheet 0.45 mm thick	297/109
b) Insulating rubber 1.2 mm thick with radioactive isotope S ³⁵	505
c) Copper sheet 0.45 mm thick	266/67
3. a) Insulating rubber 1.2 mm thick with radioactive isotope S ³⁵	517
b) Cable paper 0.12 mm thick	*
c) Core rubber 2.0 mm thick	*

¹ The numerator of the fractions is the radioactivity of the contact surface and the denominator is that of the opposite side.

mobile sulfur bonds than those of vulcanized sodium butadiene rubber. Heat treatment of rubber sulfur vulcanizates leads to a regrouping of the sulfur structures with the formation of new stronger bonds having a lower degree of sulfur. An increase of the temperature of vulcanization causes a decrease of the proportional content of mobile sulfur bonds.

In conclusion it is important to note that the method of radioactive isotopes throws new light on the study of such important technical problems as the solubility of vulcanizing and accelerating agents in various crude and vulcanized rubbers, the problem of combating sulfur bloom on the surface of rubber articles, and the question of the uniformity of dispersion of sulfur and accelerators in rubber and other mixtures⁶, insuring the manufacture of better cables.

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THE THEORY OF RUBBER REINFORCEMENT: INTERACTION OF CARBON BLACK WITH SULFUR AND RUBBER *

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One of the fundamental questions in the problem of rubber reinforcement by active fillers is the nature of the rubber-filler interaction. The commonest view on this question is based on the presumed existence of intermolecular forces at the rubber-filler boundary. Recently, however, evidence has been obtained of the possibility of chemical bonding between rubber and the commonest filler—carbon black. Thus, Stearns and Johnson¹ have shown that the differential heat of adsorption of bromine on the surface of active carbon blacks in the initial period is 28–31 kcal/mole, corresponding to the reaction of bromination of ethylene derivatives. Dogadkin and Fel'dshtejn² described as long ago as 1939 the formation of an insoluble and stable rubber-carbon gel on heating a mixture containing carbon black and sodium butadiene rubber. They attributed this to thermo-oxidative structurization processes caused by oxygen and oxygen compounds present in the carbon black. Later a number of investigations of carbon-rubber gels have been made, and Sweitzer, Goodrich, and Burgess³ have examined the mechanism of the formation from the same standpoint as Dogadkin and Fel'dshtejn². A definite correlation has been established between the reinforcing action of carbon blacks and their ability to combine with rubber. Watson⁴ and Garten⁵ consider that the formation of a carbon-rubber gel and the reinforcement effect involve the interaction of free radicals formed by the mechanical rupture of the molecular rubber chains and active centers on the carbon black surfaces. In the paper cited above, Stearns and Johnson¹ consider the possibility of bond formation between carbon and rubber in the vulcanizate through sulfur atoms. However, this hypothesis is not supported by the results of Lukomskaya and Dogadkin⁶ who showed that the dipole moment of a vulcanizate does not depend on the filler, and is the same both for filled and unfilled rubbers. Thus, the question of the nature of carbon-rubber interaction has not found a generally accepted solution and requires further investigation and discussion. Experimental data directly related to this problem are presented below.

EXPERIMENTAL

Interaction of carbon black with sulfur under the thermal conditions of vulcanization.—Two kinds of carbon black were used: channel black from Ukhta, and the same black after hydrogenation.

The purpose of the hydrogenation was to decrease the amount of adsorbed and chemically combined oxygen on the particle surfaces. The process was

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carried out in a rotary autoclave without the use of a catalyst under an initial hydrogen pressure of 200 atmospheres at 350° (the temperature was raised for 2 hours, held for 3 hours, and lowered for 3 hours.) This treatment decreases the oxygen content of carbon black (Table I) without appreciable effect on the degree of dispersion.

The carbon blacks were heated with toluene solutions of radioactive sulfur containing S³⁵ in sealed tubes at 110, 130, and 150° for 10 hours. In one series of experiments 0.06 g of carbon and 7 ml of a toluene solution containing 7.8 g of sulfur per liter was put into the tubes. In another series, 0.025 g of A100 vulcanization accelerator (condensation product of acetaldehyde and butyraldehyde with aniline) was added to each tube.

After the heating, the carbon black was filtered off and divided into two portions. The sulfur content in one portion was determined after extraction with chloroform for 80 hours until free (adsorbed) sulfur was completely removed. The completeness of extraction was checked by absence of radioactivity in the solvent. The results gave the amount of chemically combined sulfur. In the other portion sulfur was determined before extraction; the results gave the total sulfur, including the adsorbed sulfur.

TABLE I
CHARACTERISTICS OF CARBON BLACKS

Carbon black	Elementary composition, %			pH	Colorimetric number	Specific surface in m ² /g
	C	H	O*			
Ukhta channel, before treatment	92.69	1.02	4.42	3.87	21	92.2
Ditto, after hydrogenation	96.04	1.25	2.11	7.4	23	92.6

* Determined by the Unterseicher method.

The sulfur content of the carbon was determined as follows. A weighed sample of the carbon black was suspended in an alcoholic solution of shellac, placed in the counter cell, and dried to constant weight. The activity of the residue was determined with the aid of a Geiger-Muller counter, and its sulfur content was calculated from a calibration graph plotted from activity data for a residue containing a known amount of S³⁵. As a check, the sulfur content in four samples was determined by the Eschka method as benzidine sulfate. The deviation between the results of the radioactivity method and the Eschka method was in the range of 0.01–0.12 per cent.

The analytical results are shown in Table II. It is seen from Table II that sulfur reacts chemically with carbon black and, as was to be expected, the amount of chemically combined sulfur increases and that of adsorbed sulfur decreases with increase of reaction temperature. The vulcanization accelerator appreciably increases the amount of chemically reacting sulfur.

Figure 1 shows curves for the kinetics of sulfur addition to channel black in the temperature range 110–145° in the presence of A100 accelerator. The initial rate of reaction, determined from the tangent at the origin, varies in conformity with the Arrhenius equation. The apparent activation energy for the addition of sulfur to carbon black, calculated from this equation, is approximately 15,000 calories.

It is natural to attribute the increased activity of carbon black toward sulfur after hydrogenation to addition of the latter at the sites of reduction of functional oxygen-containing groups. However, we were not able to detect the evolution of measurable amounts of hydrogen sulfide in the reaction of

TABLE II
CONTENTS OF TOTAL, ABSORBED, AND CHEMICALLY COMBINED SULFUR IN DIFFERENT SPECIMENS OF CARBON BLACK HEATED AT 110, 130, AND 150° IN PRESENCE AND IN ABSENCE OF VULCANIZATION ACCELERATOR (AS % ON THE CARBON)

	110°						130°						150°					
	Hydro-generated black			Channel black			Hydro-generated black			Channel black			Hydro-generated black			Channel black		
	Without	With	Without	With	Without	With	Without	With	Without	With	Without	With	Without	With	Without	With	Without	With
Sulfur Content																		
Total content (a)	0.07	0.5	0.15	0.40	0.12	0.39	0.22	0.40	0.29	0.57	0.37	0.74						
Chemically combined (b)	0.04	0.2	0.09	0.25	0.10	0.31	0.18	0.37	0.28	0.54	0.37	0.75						
Adsorbed (extracted by chloroform) from the difference (a-b)	0.03	0.3	0.06	0.15	0.02	0.08	0.04	0.03	0.01	0.03	—	—						

* Results obtained by Eeschka method; accelerator, diphenylguanidine.

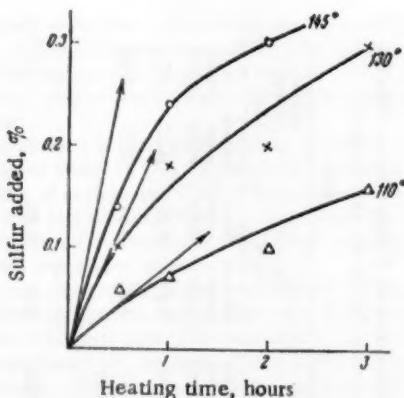


FIG. 1.—Kinetics of the addition of sulfur to channel black at various temperatures.

sulfur with hydrogenated carbon black (in a system without accelerator). The possibility of direct addition of sulfur at active sites of the carbon surface is therefore not excluded. This question requires further experimental investigation.

Interaction of carbon black with rubber.—Sodium butadiene rubber was mixed in air on laboratory rolls with approximately half its own weight of carbon black. The mixture was heated for an hour at 100° and 180° in air and in nitrogen. The amount of carbon-rubber gel was determined after extraction of the mixture by benzene in a Soxhlet apparatus for 20 hours. The results are shown in Table III. It is seen that even simple milling in air results in the binding of up to 50 per cent of the rubber in a form not extracted by benzene. The amount of bound rubber increases considerably (by about a half) as the result of heating, and heating in air leads to greater structurization

TABLE III
EFFECT OF HYDROGENATION OF THE CARBON BLACK
ON FORMATION OF CARBON-RUBBER GEL

Type of carbon black	Conditions of heating the mixture	Weight of carbon in mixture, g	Weight of rubber, g		Combined rubber, %		
			Before extraction	After extraction	Of the mixture	Of total rubber	Of carbon black
Ukhta channel black	Without heating	0.2606	0.5212	0.2076	26.5	39.8	79.5
	1 hour in air at 100°	0.4153	0.8307	0.5127	41.2	61.6	123.0
	1 hour in nitrogen at 100°	0.4403	0.8805	0.6035	45.5	68.5	136.8
	1 hour in air at 180°	0.4410	0.8820	0.7980	60.3	90.5	181.0
	1 hour in nitrogen at 180°	0.4108	0.8216	0.7038	57.0	85.5	171.0
Ditto, after hydrogenation	Without heating	0.3112	0.6226	0.3170	34.0	51.0	102.0
	1 hour in air at 100°	0.3210	0.6422	0.4648	48.2	72.2	144.4
	1 hour in nitrogen at 100°	0.3544	0.7088	0.4888	46.3	69.0	138.0
	1 hour in air at 180°	0.3042	0.6084	0.5766	63.2	95.0	190.0
	1 hour in nitrogen at 180°	0.2975	0.5951	0.5325	59.7	89.5	170.0

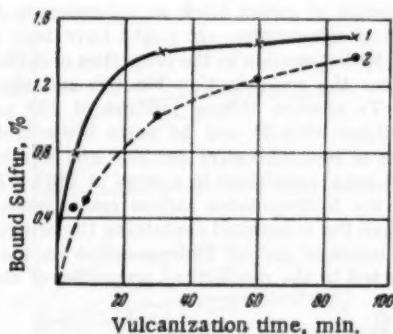


FIG. 2.—Kinetics of sulfur addition in the vulcanization of butadiene-styrene rubber in mixtures with hydrogenated carbon black (1) and untreated channel black (2).

of the rubber than heating in nitrogen. It is not possible to draw convincing conclusions concerning the mechanism of carbon-rubber gel formation from the results of these experiments, as the milling was performed in air, in conditions in which structurization of sodium butadiene could occur without chemical action with the carbon black. It is significant, however, that greater structurization of the system occurs on mixing with hydrogenated carbon black than with the original carbon before hydrogenation.

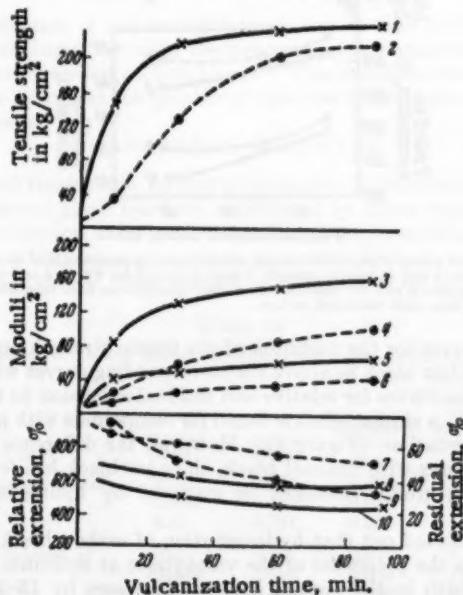


FIG. 3.—Variation of physical properties during vulcanization of compounds of butadiene-styrene rubber filled with channel black: 1 and 2) tensile strength, 3 and 4) moduli for 400%, 5 and 6) moduli for 200%; 7 and 8) relative extensions, 9 and 10) residual extensions. Continuous lines represent vulcanizates with hydrogenated, broken lines, with untreated carbon.

Effect of hydrogenation of carbon black on vulcanization kinetics and on the mechanical properties of vulcanizates.—It might have been expected that the changes produced by hydrogenation in the properties of carbon black, described above, would influence the vulcanization kinetics and the properties of the filled vulcanizates. To confirm this, a mixture of 100 parts by weight of butadiene-styrene rubber SKS-30 and 54 parts by weight of carbon black (accelerator: mixture of benzothiazolyl disulfide and diphenylguanidine) was vulcanized under the usual conditions in a press at 143°. As Figure 2 shows, the compound with the hydrogenated carbon reacts more rapidly and adds rather more sulfur than the compound containing the original untreated channel black. This influence of carbon hydrogenation on the kinetics of sulfur addition is also reflected in the mechanical properties of the vulcanized com-

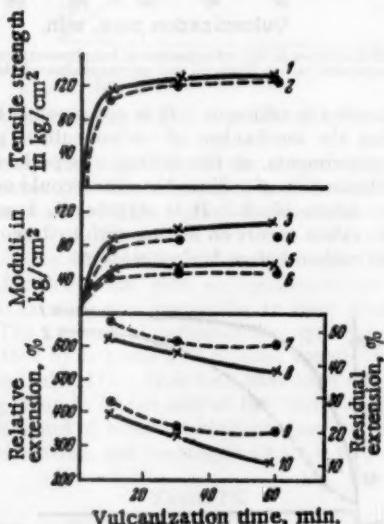


FIG. 4.—Variation of physical properties during vulcanization of compounds of butadiene-styrene rubber filled with jet black: 1 and 2) tensile strength, 3 and 4) moduli for 400%, 5 and 6) moduli for 200%, 7 and 8) relative extensions, 9 and 10) residual extensions. Continuous lines represent vulcanizates with hydrogenated, broken lines, with untreated carbon.

pounds. The curves for the variation of the tensile strength and moduli with hydrogenated carbon black lie above the corresponding curves with the original channel black; the curves for relative and residual extension lie in the opposite order (Figure 3). A similar effect is found for compounds with jet black before and after hydrogenation (Figure 4). However, the difference in this case is less than in mixtures with channel black, since jet black has fewer functional oxygen-containing groups, modified or removed by hydrogenation, on the particle surfaces.

It must be pointed out that hydrogenation of carbon black has relatively little influence on the properties of the vulcanizate at optimum vulcanization. The tensile strength in the present instance increases by 15–20 kg/cm² (for channel black). The change of the modulus is greater, which is in good agreement with the change of the combined sulfur content. The differences in the properties are leveled out if the vulcanizates are tested at 100° (Figure 5).

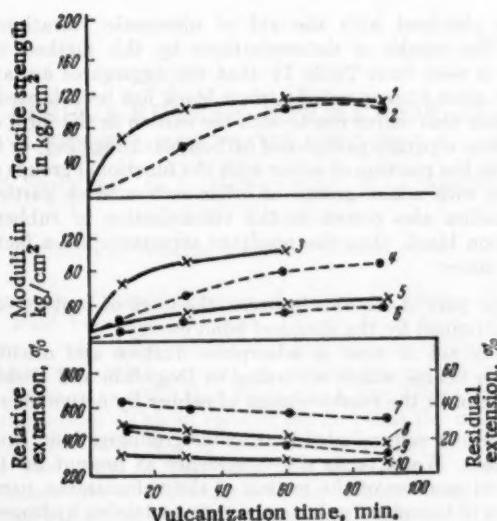


FIG. 5.—Physical properties of vulcanizates filled with channel black, at 100°: 1 and 2) tensile strength, 3 and 4) moduli for 400%, 5 and 6) moduli for 200%, 7 and 8) relative extensions, 9 and 10) residual extensions. Continuous lines represent vulcanizates with hydrogenated, broken lines, with untreated, carbon.

However, an increase of the testing temperature to 100° does not completely eliminate the difference between the properties of compounds containing untreated and hydrogenated carbon blacks. This indicates that hydrogenation of carbon black influences the number of chemical bonds in the spatial structure of the vulcanizate.

DISCUSSION OF RESULTS

An important result of the present investigation is that the chemical addition of sulfur to channel black has been established by direct experiment. It was found that the chemical activity of channel black increases after hydrogenation.

The reaction between carbon black and sulfur leads to an increase in the dimensions of the carbon black aggregates, determined by the light absorption

TABLE IV
DIMENSIONS OF CARBON BLACK AGGREGATES FROM COLORIMETRIC DATA

Type of carbon black	Color of filter	Optical density	Aggregate radius in μ	Number of primary particles in aggregate	Colorimetric number
Hydrogenated carbon black	Blue	0.511	0.035	2	28.2
	Green	0.43	0.042		
	Red	0.351	0.051		
Ditto, heated in toluene at 150°	Blue	0.45	0.040	3	24.8
	Green	0.395	0.046		
	Red	0.30	0.060		
Ditto, heated with toluene solution of sulfur at 150°	Blue	0.34	0.053	4-5	14.9
	Green	0.278	0.065		
	Red	0.25	0.072		

of suspensions obtained with the aid of ultrasonic vibrations (frequency 10,000 cps). The results of determinations by this method are shown in Table IV. It is seen from Table IV that the aggregates are approximately doubled in size after hydrogenated carbon black has been heated with sulfur. This means either that sulfur reacts with the carbon in the form of a biradical capable of binding separate particles of carbon black together, or that the thiol groups formed in the reaction of sulfur with the functional groups of the carbon black can react with active groups of other carbon black particles. If such structure formation also occurs in the vulcanization of rubber compounds filled with carbon black, then the resultant structures are a factor in rubber reinforcement, since:

- a) They bear part of the tensile stress, the work of rupture of these structures being determined by the chemical bond energy;
- b) They may act as sites of adsorptive fixation and orientation of the molecular rubber chains which, according to Dogadkin and Pechkovskaya⁷, is the principal factor in the reinforcement of rubber by active fillers.

The possibility is not excluded that sulfur groupings bind carbon black to rubber molecules. We have no direct evidence at present for this reaction; but the observed increase of the moduli of the vulcanizates, parallel with increased contents of bound sulfur in compounds containing hydrogenated carbon black, makes this reaction highly probable. In such a case the carbon black structures enter into the vulcanization network, being joined to its rubber component by chemical bonds. The extent of formation of such bonds depends both on the extent of the reaction between sulfur and carbon black, and on direct interaction between carbon black and rubber.

The entry of carbon black structures into the composition of the vulcanization network must also be considered as a factor in rubber reinforcement.

SUMMARY

Active channel black combines chemically with sulfur when heated with sulfur solutions.

The amount of sulfur combined increases after hydrogenation of the carbon black.

The dimensions of the carbon black aggregates increase as the result of the reaction with sulfur.

Hydrogenation of channel black increases the content of insoluble rubber in the carbon-rubber gel formed during milling of a rubber-carbon black mixture.

Hydrogenation of channel black increases the content of bound sulfur, the modulus, and tensile strength, in comparison with vulcanizates containing the original unhydrogenated channel black.

These facts suggest that active carbon black enters the composition of the vulcanizate structure, and this is a factor in rubber reinforcement.

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BOUND-RUBBER FORMATION IN DIENE POLYMER STOCKS *

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The phenomenon of insolubilization of rubber by carbon black has been known for at least twenty-seven years. There have been many attempts during this time to establish a relationship between insolubilization, or bound rubber formation, and reinforcement of rubber by carbon black. It was postulated, as far back as 1925, that there was a parallelism between particle size and insolubilization. This in spite of the fact that the methods available for determining particle size of very fine powders at that time were relatively crude. It was postulated at that time that there was a close relationship between the phenomena of vulcanization and reinforcement. This concept has had recurrent periods of popularity since that time.

The insolubilization of rubber by carbon black, or other pigments, has been estimated by various techniques by the early investigators in the field. In more recent work, the trend has been toward a very straightforward experimental approach. Bound rubber in an uncured rubber-filler compound is usually determined by static extraction using the same apparatus and techniques used in determining the gel content of unfilled polymers. It follows that, using this method, polymer insoluble because of crosslinking, or gel, cannot be distinguished from polymer insolubilized by incorporation of fine fillers. In investigating the formation of bound rubber, therefore, the presence of gel in the polymer being used, or formation of polymer gel during processing must be taken into account.

Although the existence of bound rubber has been recognized for some time, there has never been any widespread agreement on the mechanism of bound-rubber formation or on the nature of the bonds involved in bound-rubber formation. It was hoped that determination of the conditions required for bound-rubber formation might shed some light on the nature of the phenomenon.

Since the work was undertaken in connection with the program of the Office of the Quartermaster General on the development of elastomers for Arctic service, polymers designed for low-temperature service were used in most of this work. The study of the effect of processing conditions on bound-rubber formation was carried out largely with an experimental polybutadiene-Philblack O masterbatch (PE 911-R231MB) furnished by Phillips Petroleum Corp. The polymer used in this masterbatch was prepared at 86° F and modified to give a Mooney viscosity, unfilled, of 26.

As a starting point it seemed desirable to have a mixture of polymer and black containing little or no bound rubber. It was felt initially that a co-precipitated black masterbatch might meet this requirement. However, this

* This is an original publication of a paper presented before the Rubber Division of the American Chemical Society at the meeting in Cincinnati, May 1, 1952. See also the following paper, this issue.

TABLE I

EFFECT OF DRYING CONDITIONS ON BOUND-RUBBER FORMATION
IN AN 86° F POLYBUTADIENE MASTERBATCH CONTAINING
41.5 PARTS OF PHILBLACK O

Drying conditions	Per cent bound rubber (based on polymer)
4 days in vacuum at room temperature	0.0*
8-12 hours at 160° F	11.5*

* Both values are known to be a little low due to slight dispersion of the carbon black.

was not the case. The polybutadiene masterbatch, as received, contained about 10% (based on the polymer) of bound rubber. This insolubilized polymer was sufficient to hold the carbon black in a discrete pellet, little or no dispersion occurring during the gel test.

The occurrence of bound rubber in the unprocessed masterbatch was quite surprising initially. However, it was found later that this bound-rubber formation occurs in drying the polymer, where temperatures of about 160° F are commonly used. Drying wet masterbatch crumb at room temperature *in vacuo* does yield a polymer-black mixture essentially free of bound rubber, as shown in Table I. It was also found that static heating at temperatures as low as 180° F caused some increase in the bound rubber content of factory dried masterbatch. The experimental errors in processing these samples and determining the bound-rubber content were usually of the order of one per cent but could be considerably higher for certain processing conditions. This was particularly true for milling or heating at temperatures which caused polymer-gel formation. However, the increase in rate of bound-rubber formation shown in Figure 1 and the increase in the limiting bound-rubber formation as temperature of static heating was increased to 270° F is believed to be real. There is no question that a real increase of bound rubber content occurred under all time-temperature conditions except one-half hour at 180° F. On

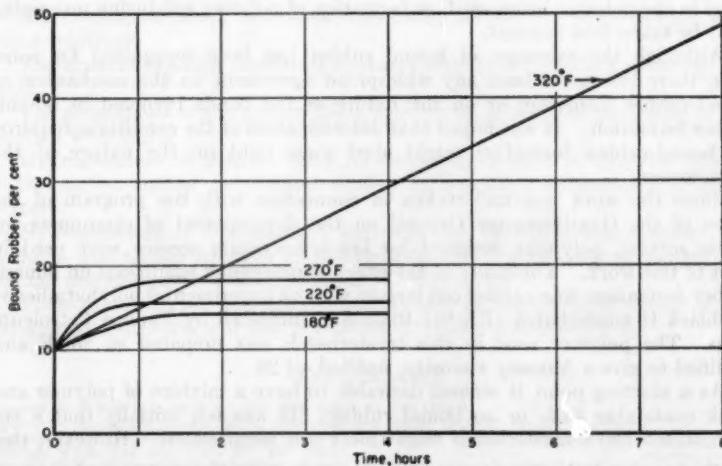


FIG. 1.—"Bound-rubber" formation during static heating of polybutadiene masterbatch.

static heating at 320° F, however, the behavior was quite different. The "bound rubber" content increased linearly with time up to eight hours and 48% "bound rubber". Static heating of a comparable unfilled polybutadiene showed that there was no gel formation below 320° F. At 320° F polymer-gel formation occurred slowly. Data on gel formation during milling of polybutadiene also showed that 320° F was a critical temperature below which no gel was formed. It appears, therefore, that the behavior of the masterbatch on heating at 320° F reflects polymer-gel formation as well as bound-rubber formation. The effects may be strictly additive in this case, but the rate of gel formation is difficult to determine accurately since the determination of low gel contents is relatively inaccurate. It does look as if the initial formation of "bound rubber" is slower than at 270° F which would indicate that the individual rates of gel and bound rubber formation are not additive.

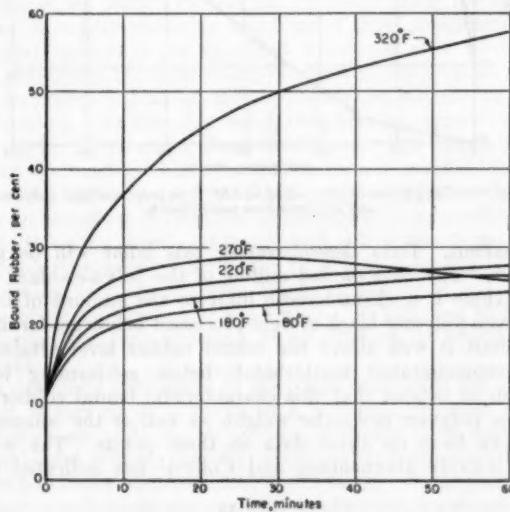


FIG. 2.—"Bound-rubber" formation during milling of polybutadiene masterbatch.

Bound-rubber formation due to milling is of course of much greater practical interest than that due to static heating. Data on this point are shown in Figure 2. It is doubtful whether there is any significant difference between the limiting bound rubber contents in this case. However, the rate of bound-rubber formation is definitely temperature dependent. Again, at 320° F, a different type of behavior is observed. Milling for ten minutes produced "bound rubber" well in excess of that produced in milling up to an hour at the lower temperatures. In this case it can be seen from Figure 3 that bound-rubber and gel formation occurring additively cannot account for the observed data. Polymer-gel formation appears to have been catalyzed by the presence of carbon black. This appears to be in conflict with the observations of other investigators who have reported that carbon black inhibits both gel formation and polymer breakdown. The gel formed in the hot milling of the black masterbatch appears to be transient, while that formed in the unfilled polymer

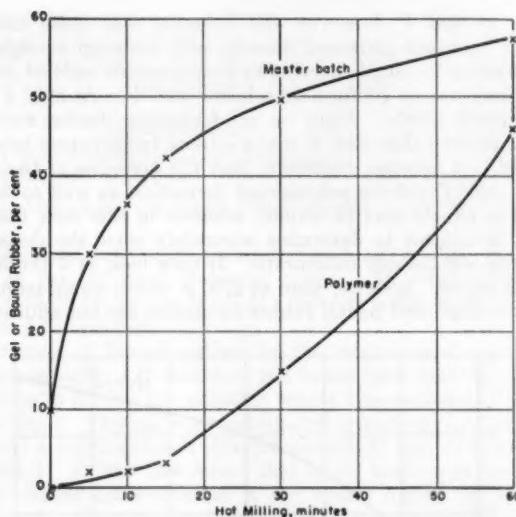


FIG. 3.—Comparison of hot milling at 320° F on polybutadiene polymer and polybutadiene masterbatch.

is more permanent. Data demonstrating this point will be given in the following paper. The data on hot milling of the polymer-black masterbatch suggests that there is a characteristic limit to the amount of bound rubber formed in a given polymer-black system processed below gel-forming temperatures. This limit is well above the bound rubber level attained by static heating the coprecipitated masterbatch below gel-forming temperatures. There is reason to believe that this characteristic bound rubber value is influenced by the polymer molecular weight, as well as the composition of the polymer, but we have no direct data on these points. The work of other investigators, notably Dannenberg and Collyer¹ has indicated that bound-

TABLE II
PEROXIDE TITRATION OF COMMERCIAL RUBBER BLACKS

Black	Type	Diameter, m μ	% "Active oxygen"
Kosmobile	HPC	20-25	1.14
Spheron 6	MPC	31 ^a	1.12
Wyex	EPC	30-35	1.21
Philblack O	HAF	36 ^b	1.10
Statex K	VFF	35-40	1.01
Shawinigan	CF	45-50	0.54
Sterling SO	HSF	51 ^a	0.88
Philblack A	HMF	59 ^b	0.80
Sterling L	HMF	86 ^a	0.88
Continox	SRF	95-100	0.53
P-33	FT	174 ^b	0.76
Thermax	MT	371 ^b	0.32

^a Surface average diameters from Cabot Carbon Blacks under the Electron Microscope, Godfrey L. Cabot, Inc., Boston, Mass., October, 1949.

^b Surface average diameters from Chemical and Physical Properties of Philblack Carbon, Phillips Petroleum Company, Akron, Ohio, Bulletin No. 246.

rubber formation is independent of the type of black, *for reinforcing blacks*, and proportional to the gross surface loading. There are indications that changing the loading of a given black gives bound rubber in proportion to the loading.

Under some conditions added antioxidant depresses somewhat the formation of bound rubber. This suggests that oxygen, probably adsorbed on the black surface, plays a part in bound-rubber formation. Chemically combined oxygen on the black apparently does not, however. We have observed that rubber-reinforcing carbon blacks catalyze the oxidation of iodide ion by atmospheric oxygen. Furthermore, the catalytic effect is roughly proportional to the surface area of the blacks. Preliminary data on this effect are given in Table II. These data are based on the amount of iodide ion oxidized in twenty-four hours in the dark in contact with carbon black. If the atmospheric oxygen is replaced by carbon dioxide no oxidation takes place, showing that the black itself is not the oxidizing agent under these conditions.

Of particular interest is the fact that Spheron-6 after devolatilization at 1000° C has essentially the same catalytic effect as the original channel black. This shows conclusively that chemically combined surface oxygen plays no role in this reaction. On the other hand, Graphon, i.e., graphitized Spheron-6, shows no catalytic effect under these conditions. The catalytic activities of Spheron-6 and the modified blacks prepared from it parallel their behavior as rubber-reinforcing blacks in natural rubber as reported by Smith and Schaffer². Further data on the effect of Graphon on the physical properties of rubber will be given in the following paper. It is sufficient at this time to say that Graphon apparently never reinforces rubber as the term is used by the rubber technologist. The parallel behavior of these blacks in reinforcement of rubber and catalysis of a chemical reaction is suggestive. In addition to this parallel it should be pointed out that Graphon forms little or no bound rubber under some conditions.

The work described here seems on the whole to support the hypothesis that bound rubber is formed as a result of a chemical reaction. The physical adsorption theory seems to be at variance with the facts that (a) Graphon does not form bound rubber, and (b) bound rubber is irreversible, as has been demonstrated previously and confirmed in our work. While there is insufficient data to support conclusively any detailed mechanism, we suggest that bound-rubber formation is polymer-gel formation initiated catalytically by carbon black. The peculiarity of bound rubber leading to the reinforcing character of carbon black is probably its concentration around the black particles. Whether the gelled rubber is combined chemically with the black is an open question, and probably not too important a question if this hypothesis is true.

ACKNOWLEDGMENT

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BOUND RUBBER AND MECHANICAL PROPERTIES OF DIENE POLYMERS *

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INTRODUCTION

There is considerable evidence that a large amount of bound rubber in an uncured carbon black-rubber stock implies improved tire-wear properties in the vulcanizate, as has been shown by laboratory abrasion tests¹⁻⁴ and by actual road tests⁴⁻⁹. In all cases, this correlation has been with different blacks. There has been very little work done to correlate the variation in the amount of bound rubber formed and the effect on physical properties of a vulcanizate for one particular black in a polymer. Our work on bound-rubber formation indicates that the bound-rubber value is not greatly affected by processing conditions where gelation of the polymer is avoided¹⁰. For this reason, it would not be possible to make vulcanizates of one particular black and polymer having widely varying amounts of bound rubber.

However, attempts were made to correlate bound-rubber formation with mechanical properties for a particular black and a particular rubber. Some factors that may affect the mechanical properties of a polymer are (a) breakdown, (b) gelation, and (c) dispersion of the black. To study these various effects, it was decided, first, to prepare vulcanizates by different processing, each having originally approximately the same amount of bound rubber in the uncured state, and then determine what effect processing conditions have on mechanical properties. Secondly, it was decided to study what effect surface activity and dispersion of the black might have on the mechanical properties.

EFFECT OF PROCESSING VARIABLES

In the study of processing conditions, three polymers were investigated. These were polybutadiene PE-911-R236, as manufactured by the Phillips Petroleum Company, GR-S X-489 (a 90/10 butadiene-styrene copolymer), and GR-S XP-212 (an 80/10/10 butadiene-styrene-isoprene terpolymer), prepared by the U. S. Rubber Company. These polymers were chosen since we were interested in improving their properties for Arctic use. The polymers were compounded with 50 parts of Philblack O, using three different processing sequences. One set of samples for each polymer was prepared by milling polymers 30 minutes at temperatures varying from 100° F to 320° F. The black was then quickly added on a cold mill and compounding was completed. A second set of samples was prepared by adding the black on a cold mill and postmilled for 30 minutes at the same temperatures used in the first series. A final set of samples was prepared by adding the carbon black uniformly during

* This is an original publication of a paper presented before the Rubber Division of The American Chemical Society at the meeting in Cincinnati, May 1, 1952.

a 30-minute milling at the same selected temperatures. The further compounding of the latter two series was carried out as quickly as possible on a cold mill. A control, compounded quickly on a cold mill, was cured and tested for each polymer. All compounds were cured 50 and 100 minutes at 292° F. Recipes used for curing of the vulcanizates are given in Table I.

Polybutadiene.—The data obtained for polybutadiene PE-911-R236, given in Table II, may be noted first. The maximum value of bound rubber is found for the condition where the black is rapidly added and then milled 30 minutes at varying temperatures. These values are equivalent to the maximum values attained for bound-rubber formation in hot milling of polybutadiene. The control sample contained only 16.8 per cent bound rubber and this low value is presumably a result of the short processing time. For the condition where the polymer is premilled before the addition of the black, and where black is added during milling, the bound-rubber values are lower than for the condition where black is rapidly added and postmilled. The variation in the bound rubber formed for the various conditions is probably due to the difference in milling time for incorporation of black. If one observes the various mechanical properties for the three processing conditions of poly-

TABLE I
RECIPES FOR CURING RUBBER-BLACK COMPOSITIONS

Ingredients	Polybutadiene	GR-S X-489 and XP-212 ^a
Polymer	100	100
Carbon black	50	50
Sulfur	2.0	2
Altax ^b	1.5	3
Zinc oxide	1.5	5
Stearic acid	—	1.5

^a The GR-S X-489 and XP-212 were compounded in a recipe previously reported by the U. S. Rubber Company.

^b Benzothiasolyl disulfide.

butadiene, one will notice that the best properties are obtained for Condition 2 where the processing is done after the black is added. In the polybutadiene polymers tested, breakdown at high temperatures before addition of black gives poor mechanical properties, especially low-temperature flexibility. Formation of gel during breakdown at 320° F affects greatly all properties. The addition of carbon black before or during breakdown stabilizes the polymers, and mechanical properties are more consistent. Best properties are obtained if black is rapidly added and then processed. The indications are, on the basis of these results, that bound rubber may be a factor in reinforcement since the best properties are obtained for conditions where large amounts of bound rubber are attained. The high values for the bound rubber obtained for Condition 2 may be a factor in dispersion and it is possible that with longer milling time, the bound rubber would increase for the other conditions.

Butadiene-styrene 90/10 copolymer X-489 and butadiene-styrene-isoprene 80/10/10 terpolymer XP-212.—The same general trend can be noticed for polymers X-489 and XP-212 as for polybutadiene, the only difference being that the changes are not quite so pronounced as for polybutadiene. GR-S X-489 polymer sample contained 15% gel as received, and this presence of gel seems to have marked the effects of the processing variables, since the stocks show a remarkable uniformity of mechanical properties. Only the sample premilled at 320° F differed from the others. The tensile strength was lowest

TABLE II
EFFECT OF PROCESSING CONDITIONS ON PHYSICAL PROPERTIES OF POLYBUTADIENE POLYMER

	Control	Processing conditions						Hot milled during carbon black addition					
		Hot milled before adding carbon black			Hot milled after adding carbon black			Hot milled during carbon black addition			Hot milled during carbon black addition		
		100	160	270	320	100	160	270	320	130	160	270	320
Milling temperature, °F	120	100	160	270	320	100	160	270	320	130	160	270	320
Per cent bound rubber	16.8	18.8	17.8	20.1	42.9*	235	160	200	280	195	210	195	215
100% modulus, psi	215	325	425	810	530	425	625	905	550	525	490	500	155
200% modulus, psi	455	870	1030	—	—	1615	905	1180	1150	980	1060	790	370
300% modulus, psi	900	1685	1030	—	—	—	—	—	—	—	1065	790	700
400% modulus, psi	1370	—	—	930	—	—	—	—	—	—	1260	1070	1070
Cure, 50 minutes at 292° F													
Tensile strength, psi	1450	1760	1450	965	630	1715	1420	1725	1555	1440	1750	1930	1215
Elongation, %	420	315	390	415	260	310	390	390	360	380	410	440	430
Hardness, Shore A	55	62	57	61	53	58	52	53	52	54	53	50	48
Abrasion index*	527	388	245	214	191	381	315	343	335	344	368	294	226
Low-temperature flexibility (Taber)*													
-40° F	75	105	60	65	70	50	35	40	30	65	70	50	45
-65° F	195	190	160	185	200	80	65	105	60	145	170	145	130
TR70, °C	-24	-29.5	-26	-19.5	-17.5	-33.5	-27.5	-30.5	-29.5	-30	-28.5	-28	-24
Cure, 100 minutes at 292° F													
Tensile strength, psi	1665	2045	1755	1295	1055	2030	1690	1905	1735	1880	1935	1745	1535
Elongation, %	360	295	300	365	285	310	365	390	355	365	355	400	385
Hardness, Shore A	57	65	58	54	55	59	54	54	53	56	55	54	53
Abrasion index	438	643	390	393	228	413	487	415	412	391	447	460	354
Low-temperature flexibility (Taber)													
-40° F	70	120	80	50	75	60	50	45	80	65	40	45	45
-65° F	135	160	100	100	165	75	65	75	60	140	125	85	75
TR70, °C	-28	-32	-27.5	-22	-21.5	-35	-28.5	-31.5	-31	-32.5	-31.5	-30.5	-27

* Indicates per cent of ASTM Standard C. Highest value indicates greatest abrasion resistance.

† Relative stiffness determined by Taber Stiffness Gauge. Lowest value indicates most flexible stock.

‡ Sample contained 32.6 per cent gel before adding carbon black.

TABLE III
EFFECT OF PROCESSING CONDITIONS ON PHYSICAL PROPERTIES OF GR-S X-489

	Control	Processing conditions							
		Hot milled before adding carbon black				Hot milled after adding carbon black			
		120	160	270	320	140	160	270	320
Milling temperature, °F	130	120	160	270	320	140	160	270	320
Per cent bound rubber ^a	37.8	42.3	42.4	41.8	36.5	45.0	44.3	41.6	43.4
Cure, 50 minutes at 292° F	280	315	310	290	300	315	310	260	290
100% modulus, psi	860	985	970	945	845	1005	960	860	875
200% modulus, psi	1815	—	—	—	—	—	—	1765	—
300% modulus, psi	—	—	—	—	—	—	—	—	1900
Tensile strength, psi	2190	1820	1745	1770	1515	1880	1885	1845	1790
Elongation, %	340	295	280	260	280	290	295	325	305
Hardness, Shore A	58	59	58	58	57	56	56	55	57
Abrasion index ^b	215	217	222	203	183	222	246	255	243
<i>Low-temperature flexibility (Taber)*</i>									
—40° F	105	80	95	80	60	55	40	75	80
—65° F	160	125	120	150	120	110	90	65	135
TR70, °C	—45.5	—48	—47.5	—45	—43	—47	—46	—47.5	—45.5
<i>Cure, 100 minutes at 292° F</i>									
100% modulus, psi	345	420	375	400	350	360	345	360	340
200% modulus, psi	1140	1280	1170	1265	1040	1200	1205	1110	1140
Tensile strength, psi	2210	1755	1785	1725	1565	1720	1780	2110	1720
Elongation, %	280	245	255	245	245	245	250	290	255
Hardness, Shore A	61	61	62	62	59	60	58	57	60
Abrasion index	214	212	216	209	207	222	245	239	218
<i>Low-temperature flexibility (Taber)</i>									
—40° F	105	95	100	80	75	60	55	50	85
—65° F	160	155	165	125	115	110	95	85	80
TR70, °C	—46	—46	—47.5	—44.5	—41	—45.5	—45.5	—47	—46.5

* All bound-rubber values shown include approximately 15% gel. Therefore, bound rubber in all samples is about 25%.

^a Indicates per cent of ASTM Standard C. Highest value indicates greatest abrasion resistance.

^b Relative stiffness determined by Taber Stiffness Gauge. Lowest value indicates most flexible stock.

TABLE IV
EFFECT OF PROCESSING CONDITIONS ON PHYSICAL PROPERTIES OF XP-212

	Control	Processing conditions									
		Hot milled before adding carbon black				Hot milled after adding carbon black				Hot milled during carbon black addition	
		120	160	270	320	140	160	270	320	140	160
Milling temperature, °F	130	120	160	270	320	140	160	270	320	140	160
Per cent bound rubber	23.1	21.8	22.0	28.4	48.0	30.1	31.1	31.2	25.2	22.4	23.5
Cure, 50 minutes at 292°F											
100% modulus, psi	325	290	295	305	415	325	370	320	330	385	360
200% modulus, psi	1105	985	940	1005	1300	1080	1155	1165	1170	1220	1235
300% modulus, psi	2375	2055	2085	2065	—	2400	2455	2400	2440	2460	2435
Tensile strength, psi	3420	3170	3100	2550	1780	3190	3320	3150	2950	3210	3210
Elongation, %	335	395	390	350	250	360	365	355	335	365	360
Hardness, Shore A	63	62	63	61	65	62	63	62	60	64	64
Abrasion index*	222	219	243	203	153	257	275	267	261	251	243
Low-temperature flexibility (Taber) ^b											
-40°F	90	90	90	125	60	75	60	40	65	80	85
-65°F	150	170	190	215	290	150	190	130	110	155	180
TR70, °C	-42	-41	-41	-40	-37	-42	-42.5	-43	-41.5	-42	-42.5
Cure, 100 minutes at 292°F											
100% modulus, psi	415	400	355	385	505	390	400	430	405	410	425
200% modulus, psi	1415	1250	1130	1260	1535	1375	1380	1385	1400	1380	1325
300% modulus, psi	2850	2510	2520	2510	—	2800	2730	2800	—	2805	2605
Tensile strength, psi	3395	3175	2905	2880	1920	3395	2890	3250	2750	3145	3270
Elongation, %	335	350	325	320	230	340	310	330	295	320	310
Hardness, Shore A	65	64	65	64	67	64	64	64	62	66	65
Abrasion index	216	222	229	193	150	272	258	258	246	245	237
Low-temperature flexibility (Taber)											
-40°F	80	75	90	80	155	70	60	60	60	100	90
-65°F	180	195	250	285	420	215	205	185	195	275	210
TR70, °C	-41.5	-41.5	-41	-40	-36.5	-41.5	-42	-42.5	-42	-41	-40

* Indicates per cent of ASTM Standard C. Highest value indicates greatest abrasion resistance.

^b Relative stiffness determined by Taber Stiffness Gauge. Lowest value indicates most flexible stock.

and the TR-70 temperature highest for this stock. However, close examination indicates here, as with polybutadiene, that the most uniform properties are attained if carbon black is first added and the stock then milled. The results are given in Tables III and IV.

Polymer XP-212 contained no gel. The physical properties of this polymer change somewhat with processing conditions, similarly to those of polybutadiene, although the magnitude of change is less. TR-70 values for this polymer varied only over a range of six degrees for a given cure time, while in polybutadiene the range was fifteen degrees.

Data on the processing of the three polymers indicate quite clearly that: (1) fast incorporation of black with subsequent mixing at moderate temperatures yields optimum properties in general; (2) high-temperature breakdown prior to the incorporation of black is to be particularly avoided, since gel is formed with an accompanying decline of tensile properties and an increase in TR70 value; (3) addition of carbon black before subsequent mixing tends to stabilize the polymer towards gel formation; and (4) it appears that polybutadiene is affected more by processing conditions than are GR-S X-489 or XP-212. Although there is no definite information on the stability of these polymers, it is known that polybutadiene is readily oxidizable and that addition of styrene to a polymer improves its resistance to oxidation. Furthermore, the polybutadiene is a lower molecular weight polymer which should make it more sensitive to breakdown.

It seems therefore, that the effect of processing conditions is due primarily to oxidation. The more readily oxidizable polymers are more affected by processing, and the addition of black in some way retards this action.

EFFECT OF SURFACE ACTIVITY AND DISPERSIBILITY OF PIGMENT ON PROPERTIES OF POLYBUTADIENE

Effect of coating Philblack O with stearic acid.—Various workers have indicated that bound rubber is caused by physical or chemical forces between the carbon black and the polymer. If so, it might be expected that surface treating the carbon black would alter these forces and have an effect on bound-rubber formation and physical properties of the vulcanizates. The surface character of a pigment may be altered in several ways, i.e., coating the pigment, chemical means, or heat treatment.

In our work, we performed some experiments that have given some very interesting results. Although it is realized that considerably more work is necessary to conclusively establish the particular trends shown by the few experiments, the results are felt to be interesting enough to report at this time.

To determine what effect coating a pigment may have on the bound rubber formed and the physical properties of the vulcanizates of a diene polymer, stocks were prepared containing 100 parts by weight of polybutadiene and 50 parts by weight of Philblack O treated in the following ways:

1. No treatment.
2. Philblack O slurried with C. P. carbon tetrachloride, filtered, and dried.
3. Philblack O slurried with a 5% solution of stearic acid in carbon tetrachloride, filtered, and dried.
4. Philblack O slurried with a 10% solution of stearic acid in benzene, filtered, and dried.

The results in Table V show that there are significant differences in bound rubber found for uncured stocks and in the properties of the vulcanizates of this stock for treated and untreated Philblack O. Coating of the black with stearic acid reduces greatly the bound rubber formed. The bound rubber changed from approximately 17% for the untreated black to 7.5% for the coated black for equal milling time. It is possible that this value might

TABLE V
EFFECT OF TREATING PHILBLACK O WITH STEARIC ACID ON
POLYBUTADIENE VULCANIZATE PROPERTIES

Treatment	None	CCl ₄ containing no stearic acid	CCl ₄ containing 5% stearic acid	Benzene containing 10% stearic acid
Per cent bound rubber	16.8	16.5	8.5	7.5
Cure, 50 minutes at 292° F				
100% modulus, psi	215	190	180	210
200% modulus, psi	455	425	405	410
300% modulus, psi	900	855	855	880
400% modulus, psi	1320	1335	1385	1460
500% modulus, psi	—	—	1915	2000
Tensile strength, psi	1450	1455	2240	2050
Elongation, %	420	420	555	520
Hardness, Shore A	55	55	57	54
Abrasion index	527	337	463	633
Low-temperature flexibility (Taber)				
−40° F	75	70	65	—
−65° F	195	180	160	—
TR70, ° C	−24	−21	−26.5	−26
Cure, 100 minutes at 292° F				
100% modulus, psi	2500	235	215	240
200% modulus, psi	655	585	530	580
300% modulus, psi	1300	1210	1150	1220
400% modulus, psi	—	—	1820	1990
Tensile strength, psi	1655	1835	2460	2180
Elongation, %	360	395	485	420
Hardness, Shore A	57	57	59	57
Abrasion index	438	342	321	905
Low-temperature flexibility (Taber)				
−40° F	70	75	65	—
−65° F	135	150	90	—
TR70, ° C	−28	−25.5	−30	−29.5

change with longer milling time, but no experiments were run to determine what change may occur. Also, treating Philblack O with stearic acid in carbon tetrachloride solution yielded a black which gave higher tensile strength than the untreated Philblack O. Modulus was decreased only slightly, possibly not too significantly. The major effect was essentially an extension of the stress-strain curve, resulting in an increase of about one-third in the breaking elongation and 40% in tensile strength. The abrasion resistance was decreased somewhat, but low-temperature properties were improved.

No study was made to determine how much stearic acid was present on the black and what the critical concentration might be.

It is known that stearic acid affects the cure, but this does not explain the change in properties in this case, since there is only a negligible change in

TABLE VI

EFFECT OF PIGMENTS ON PHYSICAL PROPERTIES OF POLYBUTADIENE VULCANIZATES. PIGMENT LOADING, 50 PARTS BY WEIGHT

Pigment recipe	Phil-black O A	Silica (Aerosil) degussa A B		Graffon A
Per cent bound rubber	16.8	21.9	17.5	0.00
Cure, 50 minutes at 292° F				
100% modulus, psi	215	360	230	55
200% modulus, psi	455	—	460	110
300% modulus, psi	900	—	720	190
400% modulus, psi	1370	—	1040	240
500% modulus, psi	—	—	1450	325
600% modulus, psi	—	—	1980	425
700% modulus, psi	—	—	—	575
800% modulus, psi	—	—	—	815
900% modulus, psi	—	—	—	1070
1000% modulus, psi	—	—	—	1510
Tensile strength, psi	1450	450	2120	1580
Elongation, %	420	200	620	1025
Hardness, Shore A	55	87	73	43
Abrasion index	527	46	147	—
Low-temperature flexibility (Taber)				
-40° F	75	—	—	—
-65° F	195	—	—	—
TR70, ° C	-24	+5	-34	-10
Cure, 100 minutes at 292° F				
100% modulus, psi	250	540	—	80
200% modulus, psi	655	—	—	150
300% modulus, psi	1300	—	—	210
400% modulus, psi	—	—	—	295
500% modulus, psi	—	—	—	410
600% modulus, psi	—	—	—	545
700% modulus, psi	—	—	—	820
800% modulus, psi	—	—	—	1150
900% modulus, psi	—	—	—	1745
Tensile strength, psi	1665	560	—	2090
Elongation, %	360	115	—	940
Hardness, Shore A	57	89	—	46
Abrasion index	438	62	—	—
Low-temperature flexibility (Taber)				
-40° F	70	325	—	—
-65° F	135	520	—	—
TR70, ° C	-28	+1.5	—	-16

modulus. A sample containing Philblack O similarly treated with carbon tetrachloride alone gave properties similar to those obtained with the untreated black.

The stearic acid-treated black may well have dispersed more readily in the polymer due to stabilization of smaller agglomerates by absorbed stearic acid.

Since modulus is practically unaffected by particle (or presumably agglomerate) size of filler, the improvement in low-temperature properties is somewhat surprising. This is particularly true, since room-temperature modulus was substantially unaffected. However, the improvement was noted in low-temperature flexibility as measured by the Taber Stiffness Gauge and in the U. S. Rubber low-temperature retraction test. These two tests do not always give parallel results, as used in this work. The low-temperature flexibility measurement was made after only a few minutes' conditioning, so that there

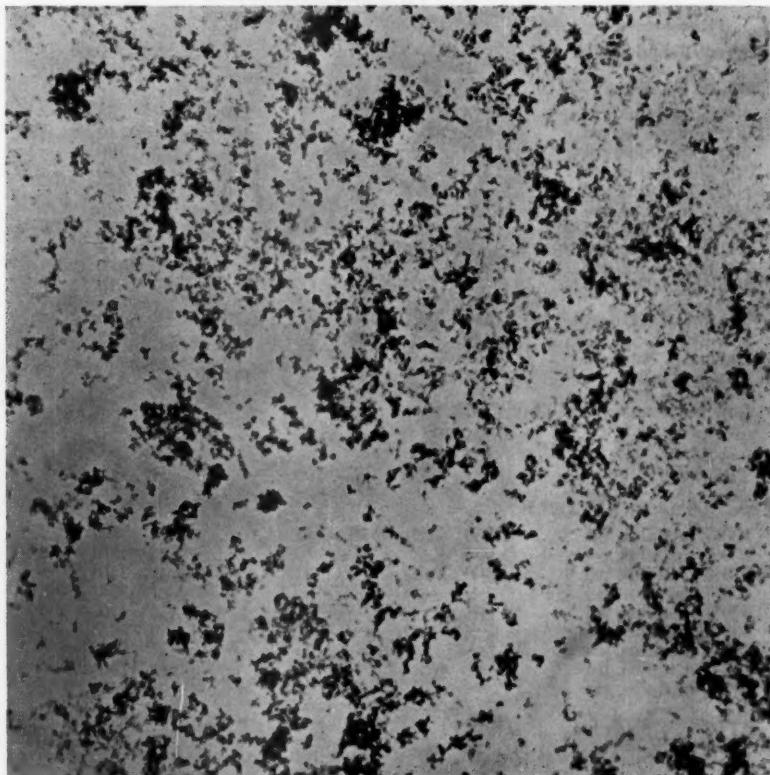


FIG. 1.—Graphon. 20,000 \times .

would be little or no crystallization. The measurement then is a determination of the second-order stiffening effect. The retraction test, on the other hand, is affected by crystallization, and is somewhat susceptible to state of cure.

EFFECT OF OTHER PIGMENTS ON PROPERTIES OF POLYBUTADIENE

It has been shown in our investigation that Graphon (a partially graphitized Spheron 6¹⁰) does not form bound rubber in polybutadiene. Also, it was shown that a silica pigment such as Silica (Aerosil) Degussa (particle diameter

of 185° and surface area of 200 m²/g, corresponding to a fully reinforcing channel black) gave approximately 20% of bound rubber with polybutadiene. If bound rubber is a factor in reinforcement, then Graphon should have no reinforcing properties and Aerosil should have reinforcing properties almost equivalent to Philblack O. The physical properties are shown in Table VI.

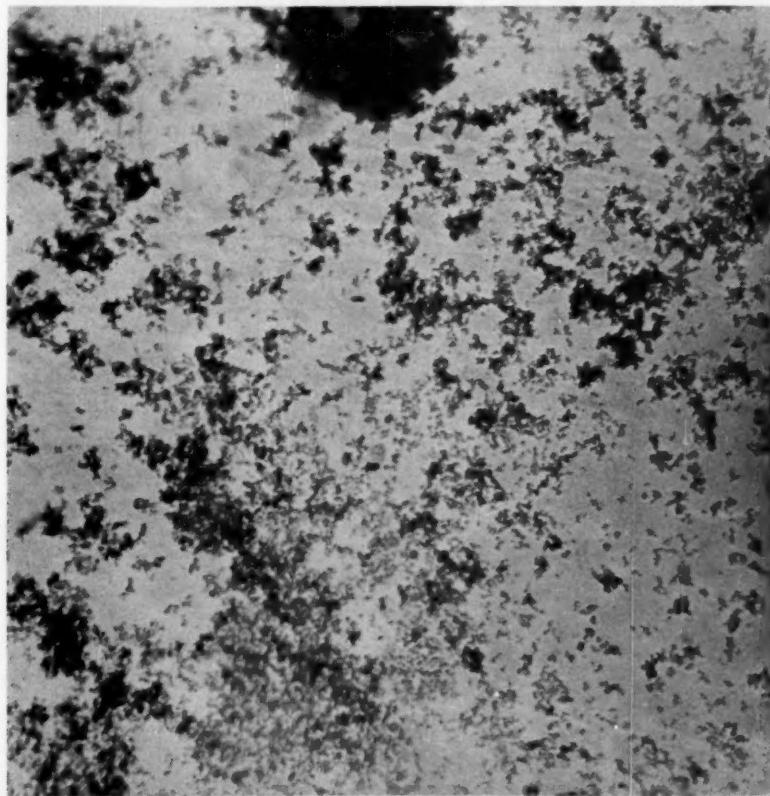


FIG. 2.—Spheron 6. 20,000 \times .

Graphon formed no bound rubber, yet produced a tensile strength higher than that achieved with Philblack O. The modulus is very low and elongation high. Abrasion resistance was not measured, since the stock was very soft, but Schaeffer and Smith have reported that in natural rubber stocks, Graphon has poor abrasion resistance. It is probable, therefore, that the modulus and abrasion resistance are correlated effects of bound-rubber formation. Tensile strength, on the other hand, is not affected by this change. The Graphon-loaded polybutadiene gave very poor low-temperature properties. The TR70 data are similar to that of a highly crystalline stock, that is, initial retraction occurs at a low temperature, but retraction increases very slowly with temperature.

It is probable that any well-dispersed fine pigment will give tensile "reinforcement", depending on particle size and possible adhesion of the rubber to the filler. Figures 1-4 show electron micrographs of dispersions of Graphon and Spheron 6. It can be seen that the particle size for both is about the same, but when added to rubber the reaction is different, as shown by the pictures having one per cent of pigment added to polybutadiene.

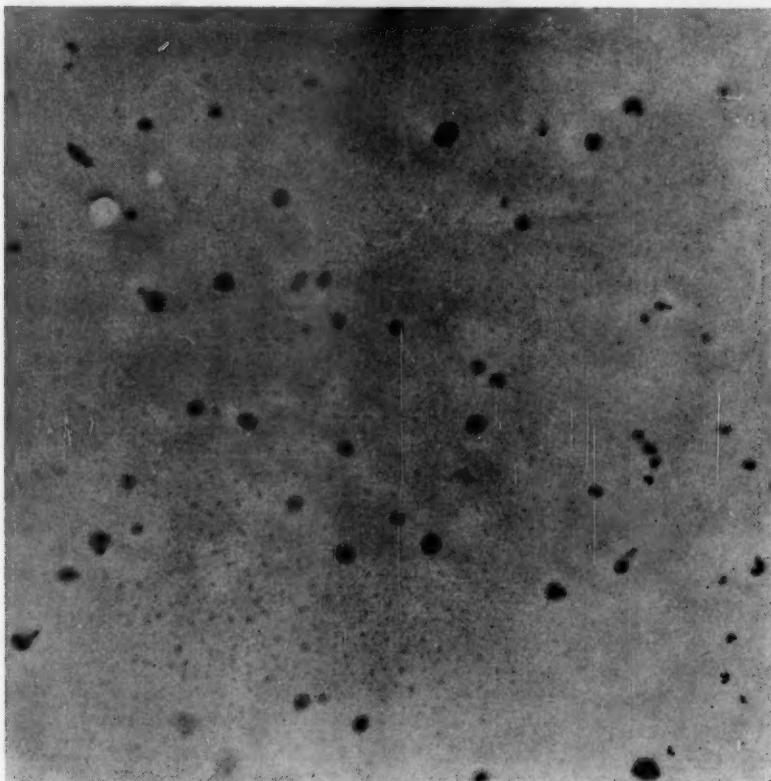
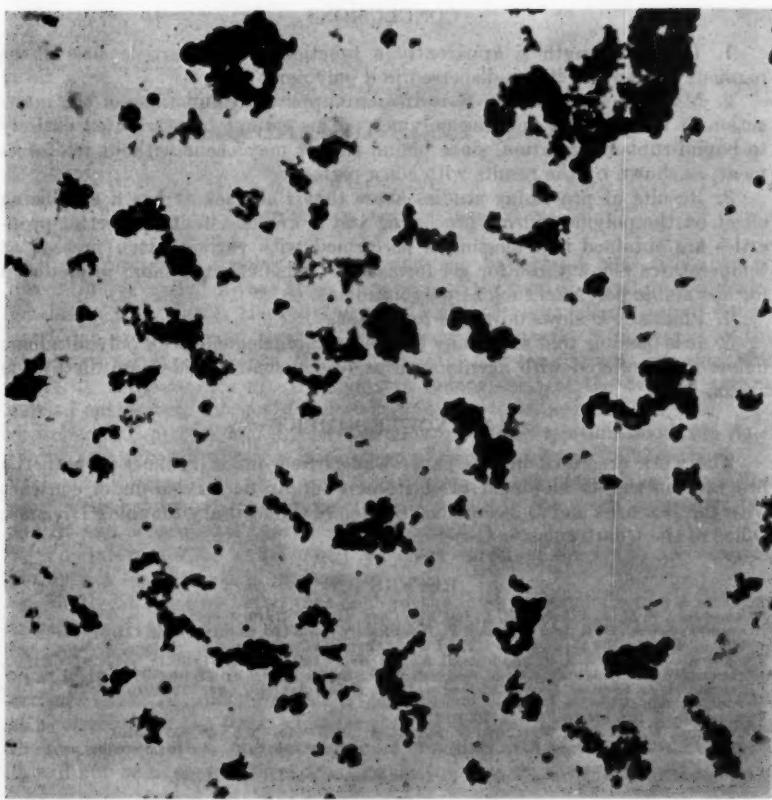


FIG. 3.—1% Graphon in polybutadiene. 20,000 \times .

On the other hand, if we observe the data for the fine silica (Table VI), we find that for Stock A we obtain no physical properties worth mentioning. This stock was cured in a recipe identical to that for the black. If the recipe is changed to one as suggested by Allen, Gage and Wolf¹¹, Table VII, we find the silica gives tensile and modulus similar to the Philblack O, higher elongation, greater hardness, and better low-temperature properties. The low-temperature property, TR-70 is improved by almost 10°. The abrasion resistance, however, is considerably lower. It is not known in this case why the properties for these two stocks should be so different. The indications are that Stock A is

FIG. 4.—1% Sepheron 6 in polybutadiene. 20,000 \times .

overcured; however, the recipe does not show any reason for this to happen, since Recipe B is the more strongly accelerated recipe. The difference is apparently tied in with the use of stearic acid, Piccolyte S-100, and diethylene glycol. These materials have either improved the dispersion of the pigment or activated the surface to induce the change. Only further work can determine the reason.

TABLE VII
RECIPES USED IN PREPARING AEROSIL VULCANIZATES

Recipe A		Recipe B	
Polymer	100	Polymer	100
Pigment	50	Pigment	50
Zinc oxide	1.5	Zinc oxide	5
Sulfur	2.0	Stearic acid	3
Altax	1.5	Sulfur	3
		Piccolyte S-100	10
		Captax	1.2
		Methyl tuads	0.15
		Diethylene glycol	3

CONCLUSIONS

1. Tensile strength is apparently a function of the particle size of the pigment and how well it is dispersed in a polymer.
2. Modulus and abrasion resistance are apparently functions of the interaction of the pigment and the polymer. This cannot be attributed entirely to bound-rubber formation, since bound rubber may occur without reinforcement, as shown by the results with silica pigment.
3. Results of processing studies show that Philblack O has a stabilizing effect on the polymer during processing and more consistent and better properties are obtained if processing is performed with carbon black present at temperatures below those for gel formation. This effect is more pronounced for less stable polymers such as polybutadiene.
4. Philblack O slows down gel formation.
5. It is possible that silica may have a destabilizing effect on polybutadiene unless it is buffered with agents such as resins, stearic acids, and diethylene glycol.

ACKNOWLEDGMENT

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CORRELATION BETWEEN LABORATORY ABRASION AND ROAD TESTING *

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In a preceding article¹, we expressed the hypothesis that probably no discontinuity exists between abrasion testing on the road and that on laboratory machines. The latter showed the peculiarity of being characterized by its very high severity. Let us recall briefly that the severity is expressed by the absolute wear of a reference mixture during the test considered. We were able to verify the existence of a relationship independent of the type of testing carried out, but a function of the severity of the tests, between the wear of an experimental mixture and a reference mixture. This relation manifests itself in different types of mixtures in the form of regressing lines. These are shown in Figure 1 where we have used logarithmic coordinates. The correlation coefficients calculated for different regressions are in the neighborhood of 0.93 to 0.95 and consequently very highly significant.

The interpretation and use of the curves shown on the graph necessitates, however, a few remarks of importance:

Firstly, it must be noted that each of the lines corresponds to a particular standard of comparison. Each of them is independent of the others. For example, for that labelled "Rubber-Resin A", the comparison rests on the wear of this type of combination rubber-resin as a function of the wear of the mixture (natural rubber containing 28 volumes of HAF black) having served as a reference for the tests, while for the line labelled "Rubber + SAF black", the reference mixture is a natural rubber containing 28 volumes of MPC black. It will not be necessary then, in any case to compare the curve for "Rubber-SAF Black" to that for "Rubber-Resin A".

Nevertheless, it is interesting to note that for comparisons where one studies the relative behavior of elastomers and not the effect of the additives (curves labelled "GR-S" and "Natural Rubber + oil") the nature and the amount of additive do not change the slope of the regression lines if the mixture is qualitatively and quantitatively the same for the two elastomers in the course of a similar treatment. In other words, the correlation confirms the independence of the effects of the polymer and of the mixture, already established by different authors.

So one might expect that the matter of proceeding, for example, in testing 5.00×15 pneumatic tires in one series of experiments then 6.70×15 in another, even on heavily loaded tires on which the absolute wear for the same distance is 5 to 10 times higher than in passenger car tires, would modify the slope of the regression lines. Such is not the case, because if the absolute wear of the reference mixture is no higher for heavy loads than in passenger car tires, the wear of the experimental mixture will be in neither case greater and the point representing the test will displace itself along the corresponding

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by John C. Park from a manuscript submitted by C. Prat and based on an article in *Revue Générale du Caoutchouc*, Vol. 34, 112-1126 (1957).

regression curve; in fact, the same form of the equation of regression $Y_1 = kY^p$ (where k and p are constants, Y_1 is the wear of an experimental mixture, and Y , the wear of a reference mixture) expresses the fact that the wear relationship, cm^3 experimental cm^3 reference (this relationship is easily derived from the curves by taking the ratio of ordinate abscissa) varies linearly with the severity of the test.

Figure 2 (already published in the preceding article) illustrates this phenomenon. Let us point out that for clarity, the experimental points have not been shown in this figure.

Finally, it may appear illogical to the reader that we have not employed in the whole of the results to which we have alluded, both in this article and in the preceding one, the same reference mixture which would have permitted

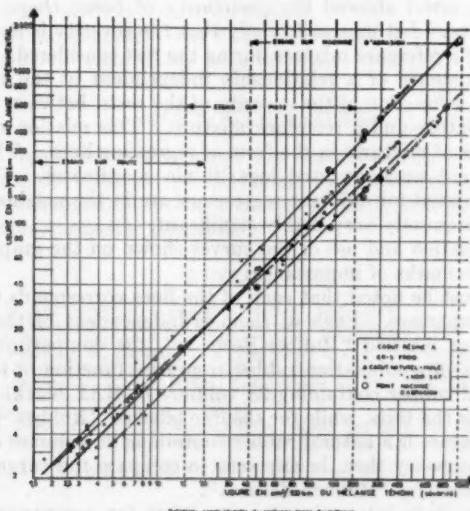


FIG. 1.—Relation between the wear of experimental mixtures (ordinate) and reference mixtures (abscisse). Essais sur machine d'abrasion means tests on abrasion machine; sur piste means on the track; sur route means on the road.

direct comparison of the different varieties of compositions studied. This is owing to the fact that the diverse comparisons which we have been conducting represented originally an entirely independent series of experiments designed to answer certain particular questions. Thus, for example, the experiments with GR-S and with oil extended natural rubber were conducted independently at the same time by the French Rubber Institute in Paris and by the Rubber Stichting at Delft (Holland). It was only after a general scrutiny of all the results obtained by these two organizations that one could bring to light the existence of the relationship "experimental rubber wear-severity". One can evidently relate by calculation all the curves of Figures 1 and 2 to the same reference mixture if one knows the flexible relationship between the different reference standards, but the comparison will thereby evidently lose some precision.

On the technical level the existence of correlation between the wear of a

rubber and the severity of testing is of interest; if one prepares a laboratory abrasion machine which renders possible variation of the operating conditions through very wide limits, it becomes possible then to calculate, beginning with the experimental points, the coefficients which determine the regressive lines "wear-severity" sought. The method of least squares, well known in statistical calculations, permits obtaining this result. Finally, by extrapolating to normal conditions on the road, one can proceed to an estimation of the behavior of a new material without having recourse to practical testing, always long and onerous.

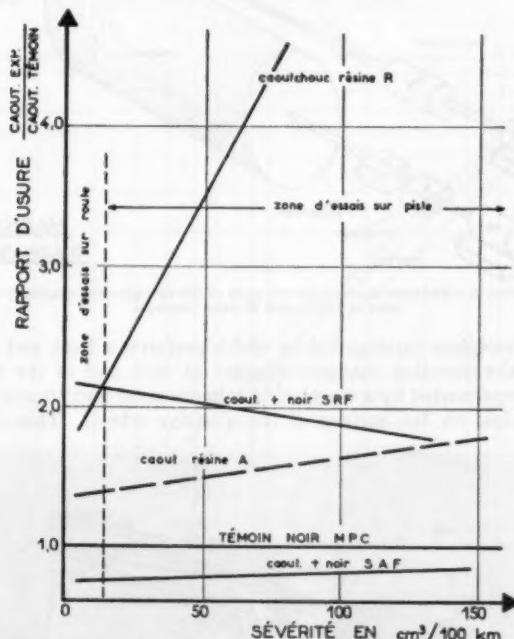


FIG. 2.—Relation between the ratio of wear of experimental rubber to reference rubber (ordinate) as a function of the severity of testing (abscissa) in $\text{cm}^3/100 \text{ km}$.

This application has been realized in a particular case at the French Rubber Institute for the evaluation and the perfection of masterbatches based upon red clay. Let us recall that there exists a natural clay, abundant on the environs of Hevea plantations, that one can introduce into latex on the spot to give a masterbatch whose interesting properties could be profitably put to use for making up rolled strips². The abrasion machine used for this work permits variation of the severity of testing at will. It was designed and built by the Technical Service of the French Rubber Institute; its principles are indicated in Figures 3 and 4.

An abrasive wheel with a diameter of 350 mm and a length of 500 mm is turned by a motor through the medium of a reducer and a variator. A 3 speed pulley system connected to the wheel, drives a master screw along which is

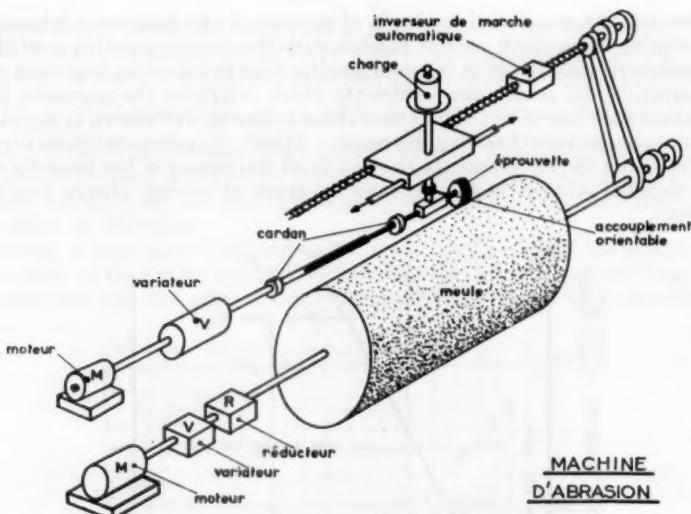


FIG. 3.—Diagram showing construction of the new abrasion machine used at the French Rubber Institute.

displaced the testpiece carriage holder which performs a back and forth movement due to the direction changers situated at each end of the wheel; thus, the testpiece represented by a wheel of 45 mm diameter and 10 mm in thickness describes a spiral on the surface of the abrasive wheel. This experimental

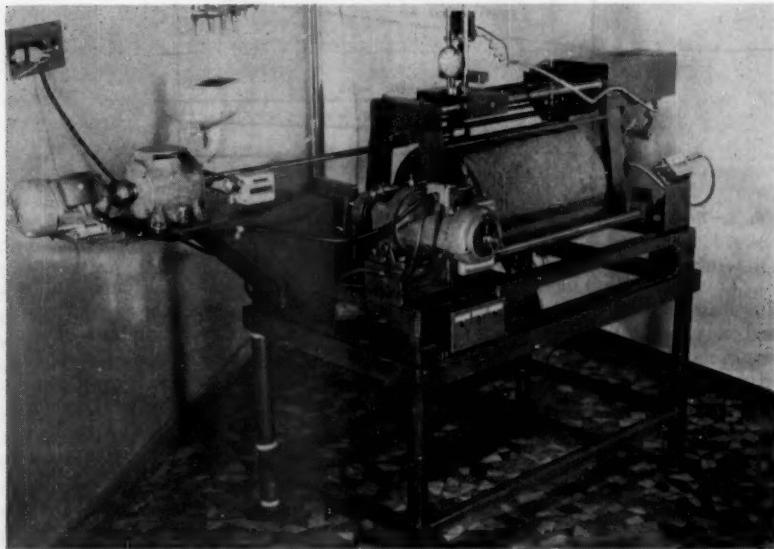


FIG. 4.—New abrasion machine on the French Rubber Institute.

wheel is controlled independently of the abrasive wheel by a motor and variator and is connected to the latter by a sliding joint and by two Cardan (flexible) joints which allow it to provide, due to the adjustable coupling which is provided the testpiece carrier, a variable angle between the axis of rotation of the wheel and that of the abrasive wheel. Moreover, the testpiece carrier can support variable loads. By combining the different variables of this machine, it is possible to cover a range of severity passing from a few dozen grams per 100 km to 1000 grams per 100 km.

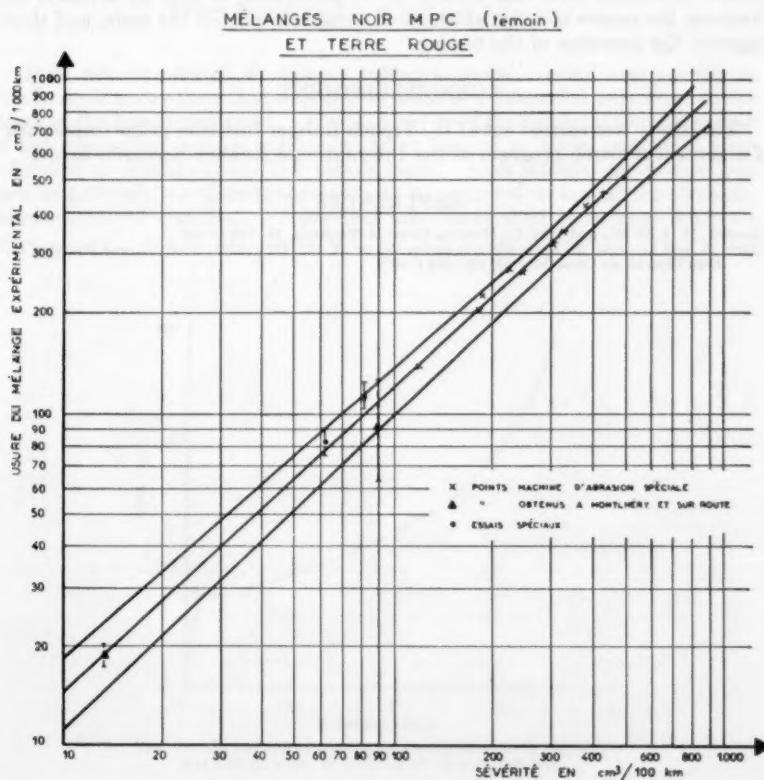


FIG. 5.—Use of the relationship between abrasion of experimental (ordinate) and reference (abscisse) mixtures for the prediction of road performance.

In the specific case of rubber based on a masterbatch of red clay, we obtained results presented in Figure 5 where the values marked by closed circles ("special tests") represent measurements carried out on an abrasion machine of the Dupont-Grasselli type. We have also illustrated on this figure the 95% limits of confidence calculated for these tests. One can state that the points ascertained from road and track tests place themselves very near the regression curve deduced from tests on the abrasion machine and that their respective limits of confidence overlap broadly.

Although one still might have a few reservations on the technical level concerning the extension of the idea of severity (one can in fact think that the mechanisms of wear which come into play on the tire are essentially different from those of a testpiece which can simulate a solid tire), the correlation established between the different methods of experimentation, road, track or abrasion machine, is probably of great technical interest since it is possible starting from simple experiments in the laboratory to obtain rapidly an estimate of the wear resistance of a new material under any conditions desired. Nevertheless, numerous tests still remain to be performed, if only to diminish or eliminate the causes of error which could come into play in the tests, and thus augment the precision of the testing.

ACKNOWLEDGMENT

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TENSION FLAWS IN BONDED CYLINDERS OF SOFT RUBBER *

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It is not uncommon to subject rubber-to-metal bonded components to tensile loads lower than that required to break a well-bonded unit as a routine check of the bonding efficacy¹. We have observed that internal fractures occur in soft vulcanized natural rubber cylinders bonded to metal endpieces when subjected to comparatively low tensile loads. Such internal flaws may well pass undetected, but their presence might be expected to impair the strength, service behavior and life. No previous account of their occurrence is known to us.

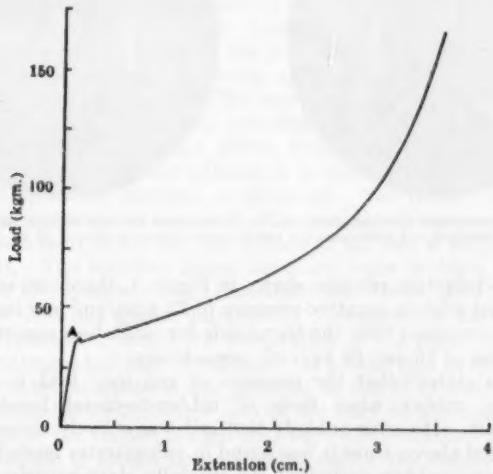


FIG. 1.—Load-extension relation for a testpiece 2 cm in diameter and 0.25 cm thick, of hardness 45° British Standard.

The rubber mixes used contained little or no carbon black, and gave vulcanizates having hardnesses in the range 30–45° British Standard. The testpieces, in the form of cylinders 2 cm in diameter and 0.07–0.50 cm in height, were prepared by a molding process and bonded by means of cements ('Ty Ply' UP and RC) to metal endpieces during vulcanization. Load-deflection relations in tension were determined using a Hounsfield tensometer, the deflection being imposed at a speed of 0.16 cm/min.

A typical load-deflection relation is shown in Figure 1. Similar relations were obtained for all the test pieces examined. Audible cracking was fre-

* Reprinted from *Nature* 180, 912–913, Nov. 2, 1957.

quently evident from the point *A* onwards, and a cross-section of a testpiece cut open after a load of 57 kg had been applied is shown in Figure 2. Several cracks about 0.3 cm in length are visible in the central region. In thinner testpieces a greater number of smaller cracks was found. The cracks often extended towards the bonded surfaces but did not appear to communicate with them, a thin film of rubber adjacent to the bond being unbroken.

It seems probable that the cracks are formed under the action of a negative 'hydrostatic' pressure, arising from the imposition of the present deformation on a substantially undilatable material, and analogous to the component of pressure proposed² to account for the load-deflection behavior of bonded units in compression. The magnitude of the negative pressure may be calculated in a similar manner; at the center of a sufficiently thin testpiece it is found to be 2σ , where σ is the average tensile traction imposed on the bonded faces.



FIG. 2.—Central cross-section of a test-piece 2 cm in diameter and 0.25 cm thick, of hardness 45° British Standard, cut open when the tensile load attains a value of 57 kg.

From the load-deflection relation shown in Figure 1, therefore, cracking seems to have occurred when a negative pressure of 23 kg/cm² was imposed. This value may be compared with the thresholds for cavitation reported³ for water and for glycerine of 16 and 63 kg/cm², respectively.

It has been stated⁴ that the presence of grit may lead to (unspecified) failures in the rubber when tests of rubber-to-metal bonded units are being carried out. It seems unlikely that grit was entirely responsible for the cracking reported above, since it was found in vulcanizates made from different batches of natural rubber, including one specially clean experimental sample.

ACKNOWLEDGMENT

This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association, and will be reported in full elsewhere.

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LOAD-DEFLECTION RELATIONS AND SURFACE STRAIN DISTRIBUTIONS FOR FLAT RUBBER PADS *

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INTRODUCTION

Rubber components comprising flat pads of vulcanized rubber secured between rigid flat surfaces are widely used as mountings and couplings. They are subjected to compression or shear, or a combination of both deformations, often of relatively large magnitude.

The shear deformation is produced by the displacement of one rigid bounding surface in its own plane with respect to the other. It differs from a homogeneous shear deformation if the pad thickness is comparable with the dimensions of the cross-section, when an appreciable bending component enters into the total deflection. The corresponding load-deflection relations have been examined by Rivlin and Saunders¹.

The compression deformation differs from a state of pure homogeneous compression in that the rubber adheres or is bonded to the rigid compressing faces and sliding at the interface is precluded. The rubber therefore bulges laterally as the deflection is imposed. The loaded surfaces are subjected to a uniform displacement, while the free surface of the pad is subjected to known stresses (zero). The resulting mixed boundary value problem has not proved tractable even for classically small displacements—its solution for large elastic displacements does not appear imminent. This problem has therefore been treated experimentally. Since the preparation of the paper, an approximate theoretical treatment has been developed. It is described in the APPENDIX.

For any rubber component the presence in use of excessive local surface strains is undesirable and a longer service life may be anticipated if the geometrical design of the surface is such that high concentrations of strain do not arise. In principle it should be possible to derive the state of strain at the surface by mathematical analysis, but in practice the problem is difficult and conclusions can only be drawn in some restricted cases. Simple measuring techniques are described whereby the distribution of strain over the surface of a rubber component may be examined experimentally. These methods have been used to determine the regime of strain over the free surfaces of some bonded rubber cylinders subjected to overall compression and extension.

COMPRESSION OF FLAT PADS

Experimental method.—Frequently, large quantities of various fillers, notably carbon black, are added to rubber compounds in order to obtain stiffer, stronger or cheaper vulcanizates. The load-deformation behavior is

* An original contribution reprinted in most part from Publication No. 265 of The British Rubber Producers' Research Association.

less perfectly elastic, however, and thixotropic effects are encountered². The present investigation was carried out with testpieces prepared using the following mix formulation and vulcanization conditions: natural rubber (smoked sheet) 100, zinc oxide 5, stearic acid 2, N-cyclohexyl benzothiazolyl sulfenamide 0.6, sulfur 2.5, phenyl-2-naphthylamine 1. Vulcanization was effected by heating for 40 minutes at 140° C. Vulcanizates of this kind may be considered as approximating to ideal highly-elastic materials³.

The testpieces were prepared by molding or by cutting from molded sheets in the form of flat pads of a range of thicknesses for each of a number of different shapes of cross-section. The cross-sections chosen were:

- (i) Square,
- (ii) Rectangular, having lengths of sides in the ratio 3:1,
- (iii) Circular, and
- (iv) Circular, with a central circular hole. The ratios of the outer and inner diameters were chosen to be 8:1, 4:1 and 2:1.

The pads were placed between sheets of emery cloth (grade 0) in a testing machine capable of exerting a compressive load of 30 tons. The load was increased from zero by regular amounts, each value being maintained for one minute before a measurement of the corresponding deflection was made.

The load-deflection relations for the stiffer pads, when large compressive loads were applied, were found to be inconsistent and to exhibit marked irreversibility. This was ascribed to stretching of the emery cloth. In some cases the emery cloth was found to have torn and corresponding cracks had occurred in the surface of the pad. Two flat steel plates were therefore machined on one surface to give sawtooth ridges, two or three thousandths of an inch in height, at intervals of about one-fiftieth of an inch. When compressed between these plates, the rubber surfaces appeared to be restrained adequately. To verify this, two thin pads were bonded to flat metal plates by means of suitable cements, during vulcanization. The load-deflection relations were found to be in good agreement with those determined on corresponding unbonded pads compressed between the machined steel surfaces described above.

The steel compression plates were wider than the widest pads, and no part of the rubber projected beyond their edges when the deflections were imposed.

Experimental results.—The experimentally-determined load-deflection relations were found to be reasonably linear for small compressions, of less than about 5% of the initial thickness, and from the slope of the linear portion a value of the apparent Young's modulus E was calculated for each testpiece. These values have been plotted in Figure 1, using logarithmic scales, against F , the ratio of the area of one loaded surface to the area of the force-free surface. For a pad of square cross-section, for example, F is given by

$$F = l^2/4lt$$

where l is the length of one side and t is the thickness. For the circular pads having central circular holes the force-free surface was taken as the sum of the two curved surfaces.

F is the shape factor proposed by Keys⁴ and Kimmich⁵ as a suitable parameter for comparing the effect of very varied cross-sections on the compressional stiffness. In agreement with this, the measured values of E are seen to lie on

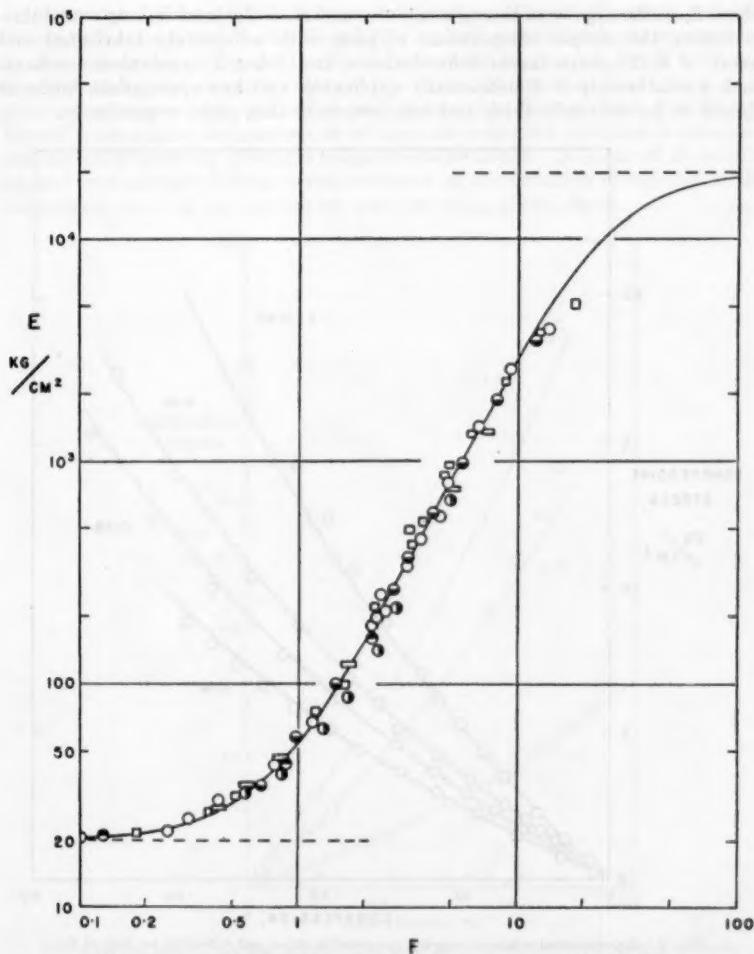


FIG. 1.—Experimental relation between apparent Young's modulus E and shape factor F for various cross-sections. The full curve is calculated from Equations (1) and (2), \square , square; \blacksquare , rectangular, with sides in the ratio 3:1; \circ , circular; \bullet , $\textcircled{1}$, $\textcircled{2}$, annular, with outer and inner diameters in the ratio 8:1, 4:1 and 2:1, respectively.

a single curve, within close limits. Some of the departures, moreover, may be ascribed to experimental errors. It is concluded, therefore, that the shape factor F provides an adequate measure of the effect of the shape of the testpiece, within the present range.

A preliminary examination of the experimental results suggested that the apparent Young's modulus E_F could be expressed by the simple relation:

$$E_F = E_0 (1 + A F^2) \quad (1)$$

where E_F is the apparent Young's modulus and E_0 is the 'real' Young's modulus, governing the simple compression of pads with adequately lubricated end faces. F is the shape factor defined above, and A is a dimensionless constant. Such a relationship is dimensionally applicable, and has appropriate limits of E_0 and ∞ for infinitely thick and infinitesimally thin pads, respectively.

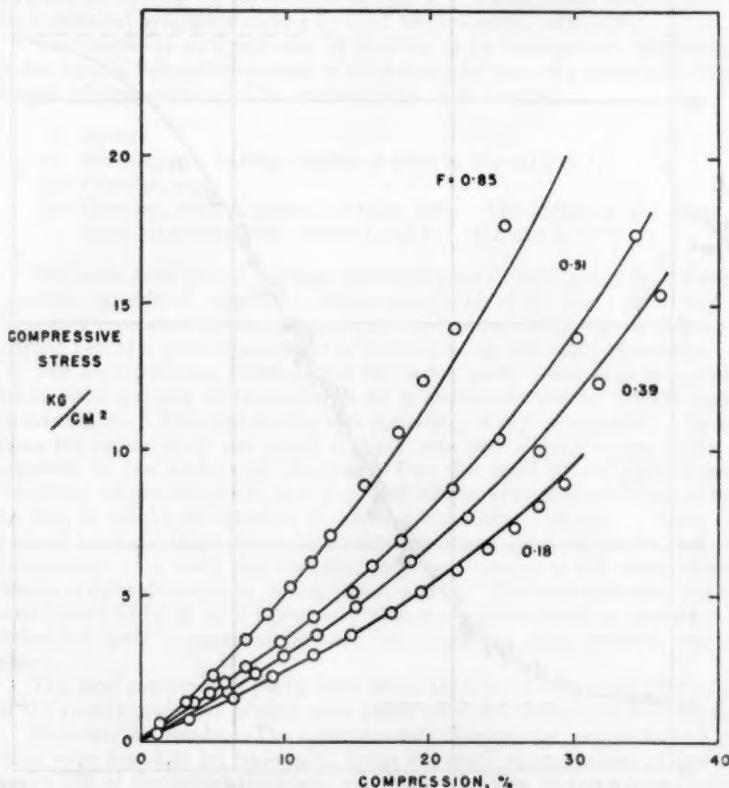


FIG. 2.—Experimental relations between compressive stress and deflection for four of the pads of square cross-section. The full curves are calculated from Equation (3).

However, for the very thin pads some contribution to the total deflection may be anticipated from bulk compression of the rubber. The deflection due to this cause may reasonably be considered as an additional contribution to that predicted by means of Equation (1), and the measured apparent Young's modulus E will then be given by

$$1/E = 1/E_F + 1/E_\infty \quad (2)$$

where E_F is given by Equation (1), and E_∞ is given by the modulus of bulk compression, about 2.0×10^4 kg/cm² for vulcanizates similar to that used in the present work⁶.

Values of E calculated by means of Equations (1) and (2), using suitably chosen values for A and E_0 of 1.75 and 20.0 kg/cm², respectively, are represented by the full curve of Figure 1. Good agreement is seen to obtain with the experimentally determined values. Moreover, the value of A used is in satisfactory agreement with that determined by Hattori and Takei⁷ and Payne⁸ from similar measurements of the load-deflection relations in compression for pads covering a smaller range of shape factor. A value of E_0 of 17.5 kg/cm² was calculated from a measurement of the modulus of rigidity of the vulcanizate used, in fair agreement with the value given above.

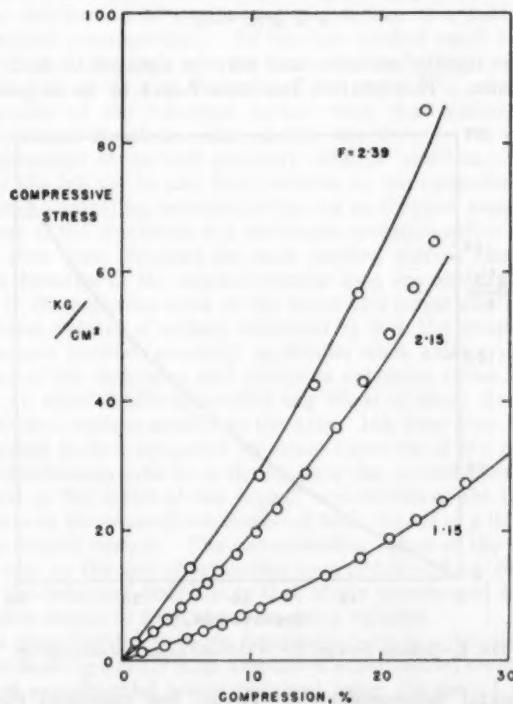


FIG. 3.—Experimental relations between compressive stress and deflection for three of the pads of circular cross-section. The full curves are calculated from Equation (3).

The measured values of E for the stiffest pads are seen in Figure 1 to fall somewhat below the values predicted by Equations (1) and (2). However, for these thin pads, slight irregularities in thickness would be expected to cause marked changes in the measured stiffness. Also the total deflections imposed were small and the experimental accuracy was correspondingly reduced. It is not certain, therefore, that the departures shown in Figure 1 are genuine.

In a more comprehensive analysis of the results presented in Figure 1 it appeared that a slightly improved agreement with the experimental results would be obtained using a relationship of the form

$$E = E_0 (1 + A' F^{1.9})$$

in place of the relationship given in Equation (1). In view of the simplicity of the latter, however, and the minor character of the improvement that could be obtained by replacing it, it has been retained as an adequate representation of the present experimental results.

In Figures 2 and 3 the load-deflection relations for relatively large compressions are presented for some of the pads of square and circular cross-sections. The kinetic theory of rubberlike elasticity predicts the following relationship between the compressive stress σ and the ratio λ of the compressed thickness to the original thickness, for a *pure homogeneous compression*:

$$\sigma = n (\lambda^{-2} - \lambda)$$

where n is the rigidity modulus, and may be equated to $E_0/3$, where E_0 is Young's modulus. This relation has been found to be in good agreement

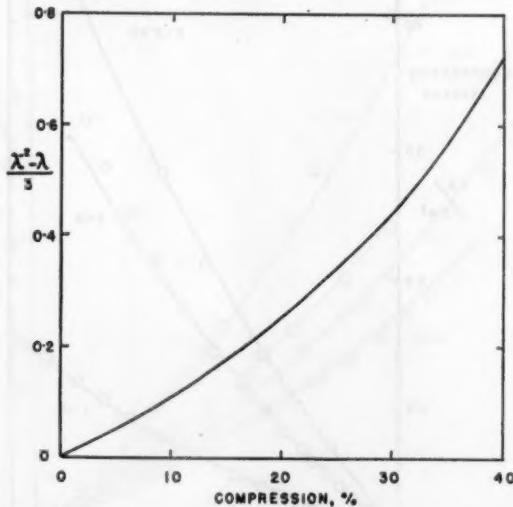


FIG. 4.—Relation between $(\lambda^{-2} - \lambda)/3$ and amount of compression.

with experimental measurements^{2,9}. Payne⁸ has suggested that the same relation may be successfully applied to the compression of pads having the loaded faces restrained from slipping, when appropriate values of E are used. The relationship becomes

$$\sigma = E (\lambda^{-2} - \lambda)/3 \quad (3)$$

where E is the apparent Young's modulus governing classically small compressions.

The full curves of Figures 2 and 3 were calculated by means of Equation (3), using values of E computed from the slopes of the linear stress-strain relations obtaining at small compressions. Fairly good agreement with the measured values of stress is seen to hold for compressions of up to 20 or 30% of the initial thickness.

It appears, therefore, that approximate values of the compressive stress for moderate compressions of flat pads may be obtained from the product of two quantities. The first, the value of E for the particular shape factor describing the pad, may be calculated by means of Equations (1) and (2) or read from Figure 1. The second, the value of $(\lambda^2 - \lambda)/3$ at the deflection imposed, is represented graphically in Figure 4.

SURFACE STRAIN DISTRIBUTIONS

Experimental methods.—Simple measuring techniques have been devised whereby the distribution of strain over the surface of a rubber component may be examined experimentally. In the first method small ink annuli were imprinted on the rubber surface in the strained state by means of a fine-drawn glass tube having an internal diameter of the order of 1 mm. Small equal circular elements on the deformed surface were thus outlined at intervals along the deformed testpiece. On relaxing the testpiece to the unstrained state the dimensions of the now generally elliptical small elements of surface contained by the ink marks and their position on the unstrained surface were measured using a travelling microscope having an eyepiece scale.

The values of the maximum and minimum extension ratios in the plane of the surface were then obtained for each marked surface element from the ratios of the diameter of the original circular area enclosed by the imprinted ink annulus in the deformed state to the minor and major axes of the approximately elliptical element of surface contained by it in the undeformed state.

In the second method, generally applicable when axial symmetry defines the directions of the maximum and minimum extension ratios in the plane of the surface, an inked regularly-toothed cog wheel of small diameter was run over the deformed surface parallel to the axis. Ink lines were thus imprinted on the deformed surface separated by equal distances of the order of 1 mm. Values of the extension ratio λ_1 in the plane of the surface parallel to the axis were obtained as the ratios of the (equal) separations of the ink lines in the deformed state to the separations measured with the aid of a travelling microscope on the relaxed surface. The corresponding values of the extension ratio λ_2 perpendicular to the axis of symmetry were obtained from the ratios of the diameter of the deformed testpiece to that of the undeformed testpiece, measured at various distances from the ends, using calipers.

Both the experimental methods described above unfortunately gave strain distributions showing a fairly large amount of experimental scatter. However, the spread of experimental points obtained using the second method is not completely random, since, due to the method of measurement, unusually high values of λ_1 are generally followed by unusually low ones. It is therefore felt that the apparently large errors may be allowed for to some extent in interpreting the results.

Compression of cylinders with plane ends.—Cylinders of vulcanized rubber bonded to plane metal endpieces were prepared using a recipe similar to that already given. The surface strains produced by overall compression were examined using the experimental methods described in the previous section. In Figure 5 the values obtained for the extension ratio λ_1 parallel to the cylinder axis are plotted against the distance of the surface element considered from a bonded edge in the undeformed state, for a cylinder subjected to several degrees of overall compression. In Figure 6 the corresponding curves are given for cylinders of various length-to-diameter ratios, compressed equally.

On increasing the overall degree of compression the distribution of λ_1 was found to become progressively less uniform, taking approximately parabolic forms at high degrees of overall compression, in this method of presentation. The local compressive strain appeared to decrease to zero, i.e., λ_1 approached

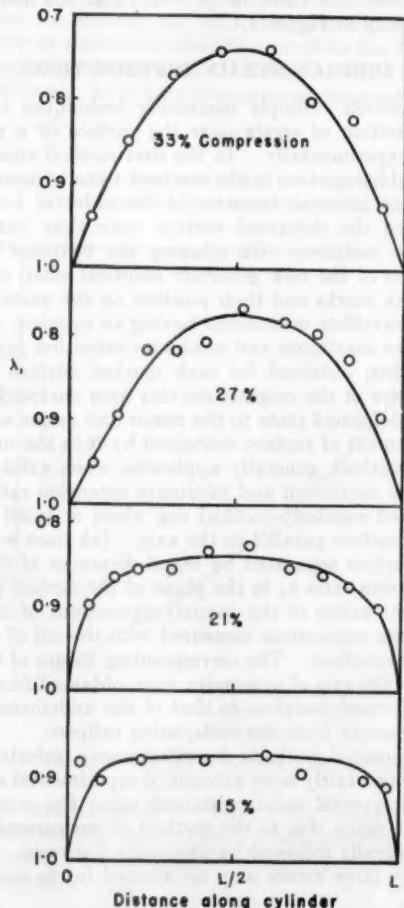


FIG. 5.—Experimental relations for the extension ratio λ_1 parallel to the axis for a bonded cylinder of length-to-diameter ratio 1.0, subjected to varied amounts of compression.

unity, on approaching the bonded edges. However, at higher degrees of overall compression or for cylinders of smaller length-to-diameter ratio, the curves were apparently displaced vertically so that tensile strains appeared, i.e., λ_1 became greater than unity on approaching the bonded edges, while the maximum compressive strain attained in the center of the testpiece surface was substantially reduced.

The values obtained for the extension ratio λ_2 in the plane of the surface perpendicular to the cylinder axis are plotted against the distance of the relevant surface element from a bonded edge in Figure 7. The values obtained for λ_2 were greater than unity in all cases, and the resulting curves had an

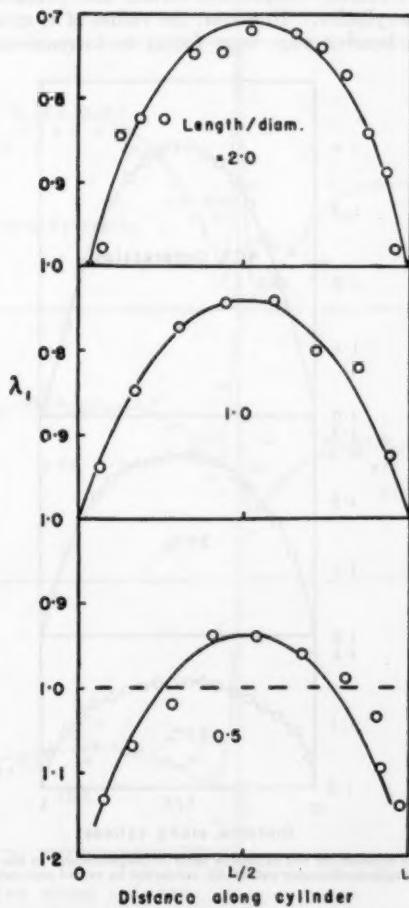


FIG. 6.—Experimental relations for the extension ratio λ_1 parallel to the axis for bonded cylinders of differing length-to-diameter ratios, compressed by 33% of the initial length.

approximately parabolic form, decreasing to unity at the bonded edges. They were obtained from, and reflect, the barrelled silhouette of the cylinder subjected to overall compression.

Extension of cylinders with plane ends.—Similar measurements have been made of the state of surface strain in cylinders bonded to plane metal endpieces and subjected to an overall tensile strain. In Figure 8, the values obtained for

the extension ratio λ_1 parallel to the cylinder axis are plotted against the distance from a bonded edge. Over a central region the distribution of strain became progressively more peaked as the imposed overall extension was increased. The variation of $(\lambda_1 - 1)$ over this central region is similar to that of $(1 - \lambda_1)$ under an overall compressive strain, and presumably reflects the limited length of the cylinder. However, the values of λ_1 measured for surface elements close to a bonded edge were found to increase indefinitely as the

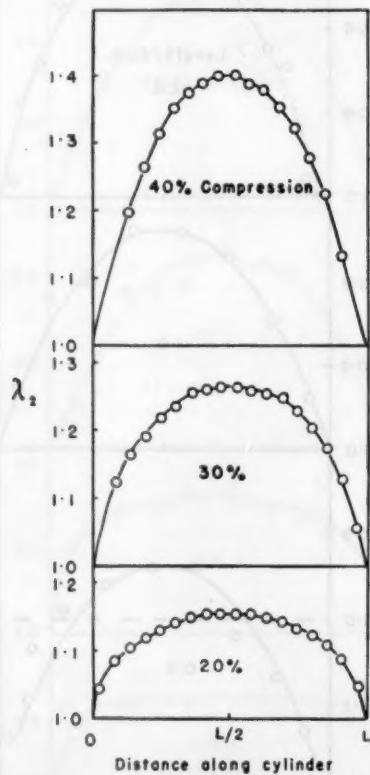


FIG. 7.—Experimental relation for the extension ratio λ_2 perpendicular to the cylinder axis for a bonded cylinder of length-to-diameter ratio 0.82, subjected to varied amounts of compression.

edge was approached. The experimental points for such surface elements have been represented by open circles in Figure 8 to indicate this feature of the results more clearly. The corresponding regions on the surface of compressed cylinders are inaccessible at high overall compressions.

The experimentally-determined values for λ_2 for a cylinder subjected to an overall extension, obtained from measurements of the waisted silhouette of the extended cylinder, are given in Figure 9.

Extension of cylinders with ends other than plane.—The surface strain distribution has also been measured for rubber cylinders bonded to metal

endpieces which are other than plane, when subjected to an overall tensile strain. The form of metal endpiece chosen is shown in Figure 10. A range of values for the dimensions a and b of the rubber 'lip' were used, and the distributions of the extension ratio λ_1 , parallel to the axis of the cylinder, on subjecting it to an overall extension were determined experimentally.

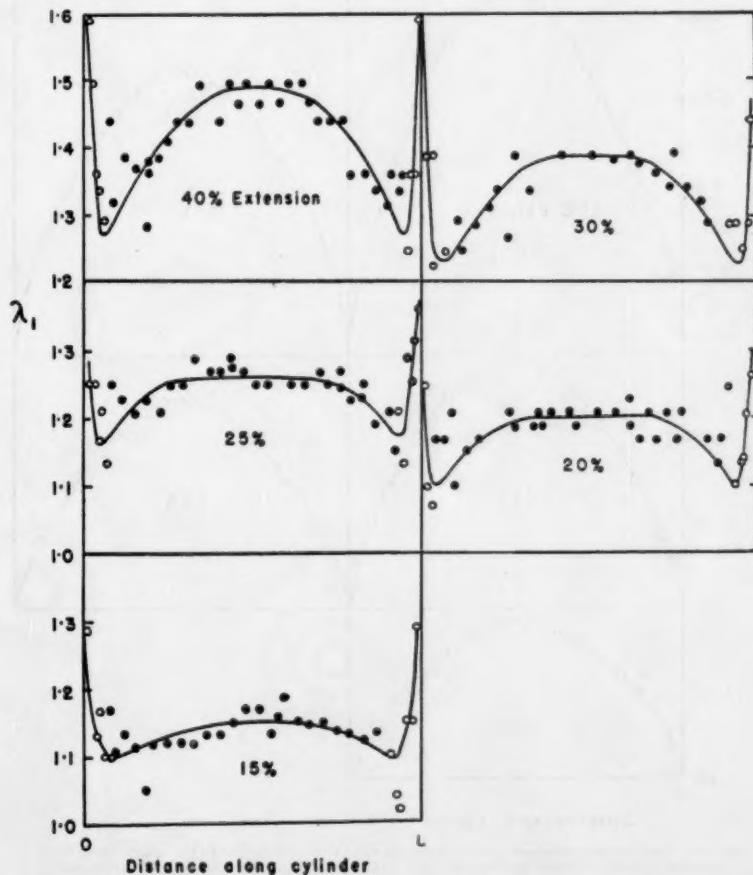


FIG. 8.—Experimental relations for the extension ratio λ_1 parallel to the cylinder axis for a bonded cylinder of length-to-diameter ratio 1.0, subjected to varied amounts of extension.

The large rise in λ_1 exhibited by cylinders bonded to plane endpieces on approaching the bonded edge, was found to be materially affected by these modifications, as shown in Figure 11 for three typical cases. For sufficiently large values of a and small values of b , the values of λ_1 were found to decrease towards unity at the bonded edge. However, for small values of b a peculiarity in the strain distribution curves was found to occur at a point corresponding

to the sharp edge of the cylindrical metal protuberance under the surface of the rubber (Figure 11). A further modification of the metal endpieces whereby the sharp edges are avoided is therefore required to produce a steady decrease in strain on approaching the bonded edge.

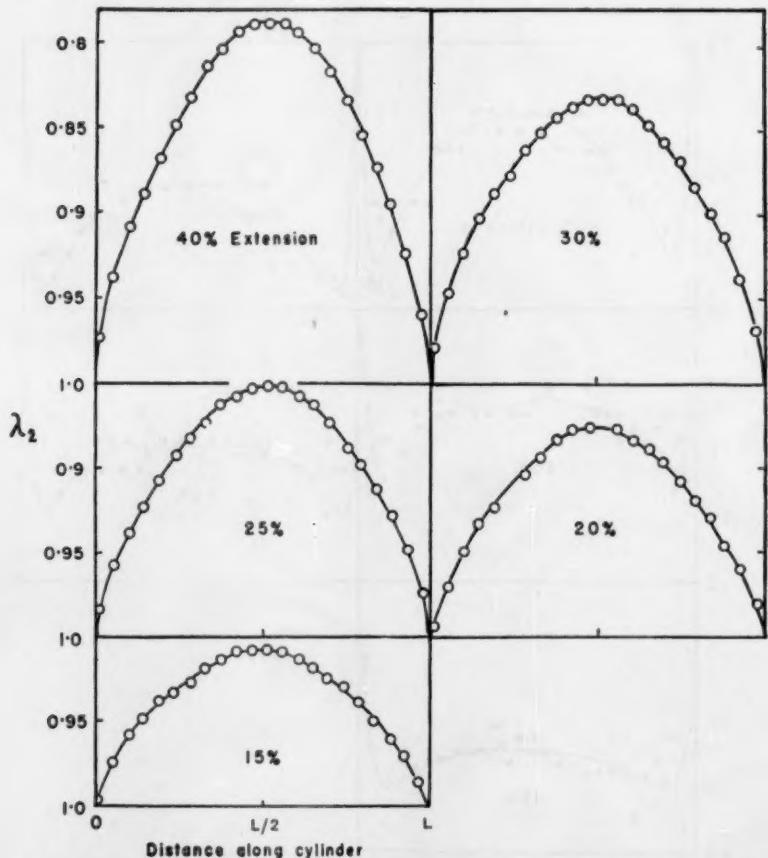


FIG. 9.—Experimental relations for the extension ratio λ_2 perpendicular to the cylinder axis for a bonded cylinder of length-to-diameter ratio 1.0, subjected to varied amounts of extension.

The dependence of the stress distribution near a bonded corner on the angle between the free and bonded surfaces has recently been examined theoretically¹⁰ for an elastic material subjected to classically small strains. Below a critical value of the corner angle the stress components have been shown to decrease to zero as the corner is approached, while for corner angles exceeding the critical value the stress components may increase indefinitely. For an incompressible material in a state of plane strain, for example, the critical value of the corner angle is found to be $\pi/4$.

The observed mitigation of surface strain in the neighborhood of the bonded edge of a solid cylinder, occasioned by modifying the metal endpiece, seems to be an analogous effect since the modifications have been such as to reduce the effective angle between the free and bonded rubber surfaces.

SUMMARY

Experimental measurements are described of the load-deflection relations for flat rubber pads in compression. They are shown to be in fair agreement with a simple empirical relationship for a wide range of thicknesses and for varied shapes of cross-section.

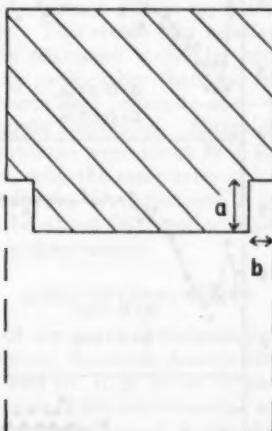


FIG. 10.—Cross-section of modified metal endpiece.

Simple measuring techniques are described whereby the distribution of strain over the surface of rubber components may be examined experimentally. These methods have been used to determine the state of strain of the free surfaces of some bonded rubber cylinders subjected to overall compression and extension.

APPENDIX

An approximate theoretical solution has been obtained for the stiffness under small compressions of a bonded rubber pad. The deformation is assumed to consist of two components—a simple compression, and a shear such that points in the plane of the bonded surface regain their original positions.

The first deformation may be maintained by a uniform compressive stress, given by $4E_0e/3$ for a pad in a state of plane strain, i.e., which is infinite in length, and by E_0e for a circular pad, where E_0 is the Young's modulus of the rubber and e is the imposed compression.

The second deformation may be approximated by a parabolic outwards displacement of an originally vertical section. The maximum outwards displacement k , midway between the bonded surfaces, will be given by the requirement that the volume within the section in the deformed state is equal to the volume contained within it in the undeformed state. Hence, con-

sidering a section at a distance x from the center of the pad, k is given, to a first approximation, by $3ex/2$ for an infinitely long pad, and by $3ex/4$ for a circular pad.

In a small element of width Δx , the small parabolic displacement of maximum amount k may be maintained by the action of one face of a uniform hydrostatic pressure ΔP , given by $\Delta P = 8E_0 k \Delta x / 3t^2$, where t is the thickness

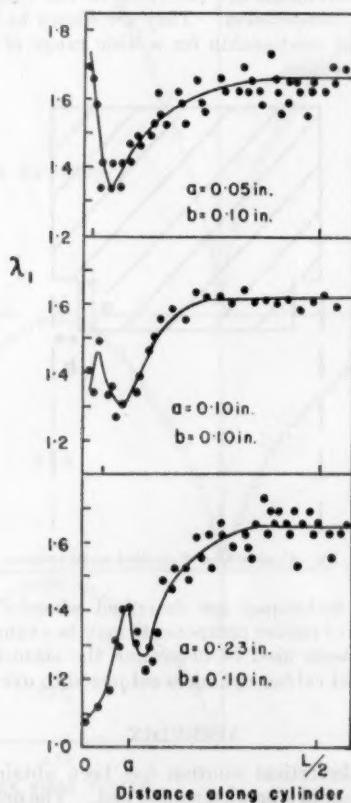


FIG. 11.—Experimental relations for the extension ratio λ_1 parallel to the cylinder axis for cylinders of length-to-diameter ratio 2.0, having modified bonded faces, extended by 56% of the initial length.

of the pad. On integrating between the free surface, where the pressure is zero, and the section at x , the value of the total hydrostatic pressure P acting at a distance x from the center of the pad is obtained. The pressure P will act on the bonded surfaces also. By integrating such terms as $P dx$ over the whole pad the corresponding compressive force that is necessary to apply to the bonded surfaces to maintain the second deformation may be calculated.

The total compressive stress may be considered as the sum of the two components; the corresponding apparent Young's modulus for the pad is

finally obtained in terms of the shape factor F , the ratio of one loaded area to the force-free area of the pad, as

$$E = E_0 (1.33 + 1.33F^2)$$

for an infinitely long pad, and

$$E = E_0 (1 + 2F^2)$$

for a circular pad.

The relation found empirically to represent the experimental results was $E = E_0 (1 + 1.75F^2)$, and is seen to be of the same form as the theoretical relations, with a numerical constant similar to, but slightly smaller than, that predicted for circular pads. This seems very satisfactory.

The long narrow pads examined would be expected to agree with the equation for infinitely long pads rather than the equation for circular pads, but the ratio of length to width used—three-to-one—was probably insufficiently large to approach plane strain conditions. Kimmich⁵ has reported that pads with sides in the ratio ten-to-one were about 22% softer than circular pads of the same shape factor, i.e., with the same ratio of loaded area to free area, of 2.0. Inserting this value in the two equations, it is found that an infinitely long pad is predicted to be about 26% softer than a circular one, in good agreement with Kimmich's observations.

ACKNOWLEDGMENTS

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DISCUSSION

DR. D. M. DAVIES (*University of Nottingham*): The first point which struck me about the paper was that the author had not done himself justice in the choice of a title. He calls it 'Load-Deflection Relations and Surface Strain Distributions for Flat Rubber Pads'. On reading the paper, I found with pleasure that it was not confined to what I would regard as a flat rubber pad and that he had covered a wide range of shape factors. To me a flat pad conjures up something like a writing pad.

The author said that a theoretical solution does not appear imminent and he has had to resort to an empirical approach, the kind of approach of which

we, as engineers, are very fond. In fact, we might well make an engineer of the author. By means of this empirical approach, he arrives at Equation (1), which I think should turn out to be a valuable guide for designers of rubber components in compression.

Equation (3) again appears to be a very valuable contribution to designers, but there is one point which disturbs me in putting this equation into practice. In attempting to calculate compression, or the stress due to compression of 30%, which is the order shown in Figures 2 and 3, you have to make use of the slope of a line established over only 5% of the compression, so that you are performing an act of faith. Nevertheless, I agree that it will be a useful guide to designers.

In the second half of the paper the author discusses surface strain distributions, and here the shapes of the curves would surprise no one, but in putting magnitudes on the curves the author has made a valuable contribution. The one snag is that the values near the ends of compression testpieces are probably the most important but, as often happens in practice, it is here that the readings are very difficult to obtain. Has he tried any other methods of getting readings in this region? Would it be possible to throw a silhouette of the specimen on to a screen and get a measurement from that, or even to use a photograph?

One important question facing designers is the elimination of regions of high stress and strain, and the author has touched on this important issue. In Figures 10 and 11 he shows one method of relieving stress—or in this case strain—concentrations. The next obvious step from Figure 10 appears to be towards a curved face, but from an engineering point of view the cost of manufacture would have to be weighed against the advantages of stress relief.

The author should be congratulated on tackling what is a very difficult problem and facing these difficult issues.

DR. GENT: Thank you for your comments. We hope that it will not be necessary for measurements to be made at small compressions in order to determine the effective Young's modulus. My colleague, Mr. Lindley, who was associated with this work, is proceeding with an attempt to correlate the Young's modulus at small compressions with some more easily determined quantity for the rubber compound, which will remove that burden. For unfilled vulcanizates, of course, the value of Young's modulus may be readily obtained from other measurements.

How can one determine the state of strain very close to the bonded edge of a cylinder in compression? We have tried taking silhouettes and photographing them, but the difficulty is that at moderately high compressions of a cylinder bonded to endpieces of the same diameter, the rubber folds over on itself and the region in which one is most interested is completely obscured and inaccessible. One has to distort the object seriously in order to be able to see the point on the surface in which one is most interested. For that reason we had to abandon measurements in compression near the bonded edge.

MR. A. R. PAYNE (*Research Association of British Rubber Manufacturers*): I congratulate the author on his paper and thank him for the invitation to contribute to the discussion. Most of what I have to say will confirm his work, because we have been engaged on a similar program at the Research Association^{1,2,3}, but there is one small point at issue which I will leave until later.

The equations we have obtained are very similar to those which the author obtained, except that I started with σ equals $E_0(\lambda\Phi)$, where Φ is a function of

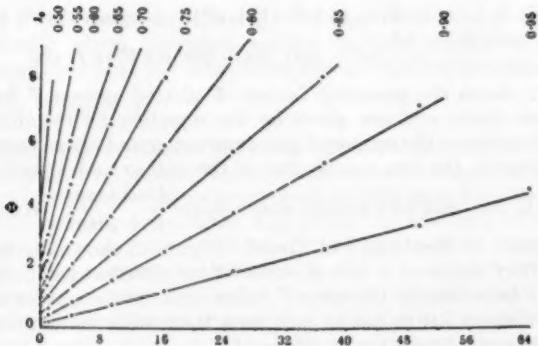


FIG. 12.

λ and shape. For lubricated rubbers of all shapes, the stress strain relationship is: $\sigma = E_0(\lambda - \lambda^{-2})$. Providing there is adequate lubrication, it means that we can measure the true modulus, E_0 .

For bonded cylinders, our relation is similar to the compound equation suggested by the author: i.e., $\sigma = E_0(\lambda - \lambda^{-2})(1 + \kappa\delta^2)$, where κ is a constant (0.413), and δ is the ratio $\frac{\text{radius}}{\text{height}}$.

For square blocks we have exactly the same relation, except that κ is 0.525 and δ is the ratio $\frac{\text{width}}{2 \times \text{height}}$.

Rectangular blocks produce a slightly different problem, and the relation found is: $\sigma = E_0(\lambda - \lambda^{-2})(A + B\delta^2)$. A and B are functions of width and length, δ is the ratio $\frac{\text{width}}{2 \times \text{height}}$. For a circular cross-sectional flat pad with

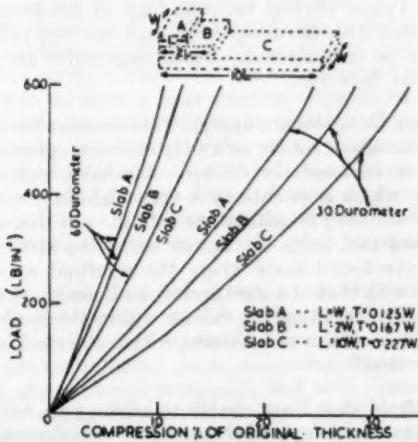


FIG. 13.

a central hole it is: $\sigma = E_0(\lambda - \lambda^{-2})(1 + \kappa\delta^2)$. κ equals 0.413, δ equals the difference of radii ($r_2 - r_1$) for r_2 very much greater than r_1 etc. height

Figure 12 shows the geometry factor— Φ plotted against δ^2 for cylinders. The plots are linear and are given by the equation for cylinders (above)¹. They were linear over the ranges of precompression and shape factors studied.

In this respect, the two approaches of the author and myself are exactly similar, but he has used as a general shape factor $\frac{\text{load area}}{\text{free area}}$. Many years ago this was criticized by Hirshfeld and Piron⁴. Figure 13 shows the basis of their criticism. They cut from a slab of rubber three different length-width thickness ratios to have exactly the same F value factor as the author used, in two different hardnesses but as can be seen from the load deflection plot there is a distinct difference between the results.

When this is plotted on the log scale which the author has shown the difference is about the scatter of his experimental points and is thus obscured. Thus although on a broad log scale, the definition F^2 will give reasonable values, when it comes to a little more detail, the universal curve shown by Dr. Gent falls down when the length-width ratio of the rectangle becomes very large. At RABRM we have studied various shaped sections both statically and dynamically, and in the main the conclusions of Dr. Gent can be adopted for the calculations of a dynamic oscillation about a static point^{1,3}.

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DR. GENT: Thank you very much. It is most valuable to have this confirmation. When the pads have a rectangular section of fairly large length-width ratios—Mr. Payne showed them as high as ten-to-one—the empirical relation must be used with circumspection and becomes rather approximate; errors of 20% may be encountered. These departures are predicted by the theoretical treatment, however.

MR. W. H. EDWARDS (*Ministry of Supply*): This question involves the extension of his subject into the use of rubber as a fully enclosed spring stressed up to the yields of steel which enclosed the rubber. We have found several uses for this type of spring, which is essentially a very high duty spring and involves pressures up to 30–40 lb/sq in within the rubber. In this use rubber has an advantage over steel and holds six to ten times the strain energy per unit volume, but we have found cases where the resultant aging life is reduced seriously compared with that of a steel spring, and one of our main troubles has been the difficulty of lubricating the rubber within the steel cylinder. Could the author suggest some form of lubricant within the steel cylinder—between the rubber and the steel?

DR. GENT: I am afraid that I am unable to advise you, but Mr. Payne may be able to help since he has carried out some experiments with rubber in compression against lubricated plates.

MR. PAYNE: The stress-strain relations have been obtained experimentally for rubber pads with silicon lubricant applied to their compressed faces. On analysis it was found that the lubrication was quite adequate.

MR. EDWARDS: Thank you.

MR. L. MULLINS (*British Rubber Producers' Research Association*): The author has described a very interesting development in our attempts to describe the elastic behavior of rubber. Here he has been ambitious and tackled a problem which is mathematically intractable, and which has not been solved for elastically simpler materials such as metals. He has also been modest, in that during recent years a great deal of work in which he himself has played no small part has been carried out to find the answer to such questions as 'If I apply a given system of stresses to a piece of rubber, what will be the resultant strain', and exact solutions are now available for a range of practical problems. I would like to comment on this for a few moments as it is possible that a number of people present are not familiar with all that is going on in the field of rubberlike elasticity.

The basis of most engineering practice is on the classical theory of elasticity which is adequate for materials in which the maximum deformation is small, but which is inapplicable to rubber except in applications where the strains are small which is of course quite an unimportant use of rubber.

A theory of rubber elasticity has been developed which gives the necessary foundation for dealing with a number of practical problems in rubber engineering. This theory has resulted from the happy synthesis of a general mathematical theory of elasticity for large strains and a study of rubber from the molecular viewpoint.

Here we have a theory of considerable power and scope which in principle is capable of giving exact solutions for a range of practical problems. Unfortunately there are two snags. The first is the limitation of our mathematical equipment and the difficulty is to develop methods of mathematical analysis suitable for the particular problem in hand. Dr. Gent has described a problem of this type where as yet is not possible to obtain an exact solution from theory, but he has shown that even though the mathematics may not be adequate the theory is still capable of giving a good guide to the behavior anticipated and thus gives indications of lines of empirical approach.

On the credit side we have a large number of problems where there is an exact solution. The author has mentioned a number of them such as simple extension, compression, and shear, torsion of a cylinder, torsion and simultaneous extension of a cylinder, torsion of hollow cylinders, torsion and axial loading of bushes, flexure of thick sheets, flexure of sheets reinforced with cords. All these and other problems are capable of exact solution, and I think you will agree represent a substantial proportion of problems which occur in practice.

The second snag arises from the extent to which theory represents the behavior of a particular rubber. If the rubber is reversible, incompressible and isotropic then the theory is applicable but any departures from these conditions introduce limitations. In a surprising number of cases rubber behaves quite well and conforms reasonably well with these conditions. You will see we have a young but robust technology of rubberlike elasticity. Perhaps the author would say something about the problems to which we have exact solutions of the elastic behavior.

DR. GENT: It is not to be expected that the range of solutions available for large deformations is as extensive as that given by classical elasticity theory where the deformations are sufficiently small substantially to simplify the mathematical treatment. But the number of problems which can be solved for large deformations, where no restrictions are placed on the magnitude of the displacement, is surprisingly large. An even larger number of solutions can be obtained in the form of second approximations, where the deformations are not classically small but a restriction is placed on their magnitude.

MR. A. BRANDER (*British Steel Piling Co.*): Mr. Payne has said that the formula which the author has developed could be modified quite easily for dynamic applications. The author says that most of the components are for dynamic applications. It would therefore be reasonable if we could be given some idea how a rubber will behave under dynamic load.

DR. GENT: There is nothing peculiar about the dynamic compression of rubber. It is now possible to predict, from the shape of the pad and the value of Young's modulus for the rubber used, the static stiffness of the pad, and in a similar manner the dynamic stiffness may be calculated if an appropriate value of Young's modulus is employed. Values of the dynamic modulus (and damping) may be obtained by observation of the dynamic behavior of vulcanized rubbers, for insertion into the relation given in the paper. A large volume of work has been carried out on the behavior of rubber under vibration, and it seems now both possible and practicable to predict the stiffness of a pad of certain typical vulcanized rubber compounds of any shape and at any frequency.

THE STRUCTURE OF CYCLIZED POLYBUTADIENE *

J. REID SHELTON AND LIENG-HUANG LEE

CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO

INTRODUCTION

Natural and synthetic rubbers are converted to resins upon heating with polar catalysts of the Friedel-Crafts type, and with certain acids^{2,3,8}. The reaction is generally considered to involve an isomerization in which segments of the linear chain are converted to rings, and consequently the product is called cyclorubber.

Information bearing on the structure of cyclorubber has been reviewed by D'Ianni² and Gordon^{6,6}. The formation of a six-membered ring appears to be well established^{11,12}. van Veesen¹³ has presented evidence based on changes in amount and type of unsaturation, as measured by hydrogen chloride addition, which suggest the formation of "condensed polycyclohexyl groups" connected by shorter or longer polyisoprene chains. Gordon⁷ considers that such structures "are achieved at most in negligible amount". Rao¹² determined unsaturation in cyclized rubber using phenyl iododichloride and obtained values in close agreement with theoretical values predicted by Flory and Gordon and significantly different from those obtained by van Veesen using hydrogen chloride.

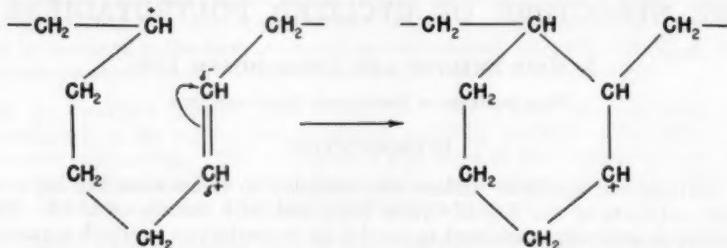
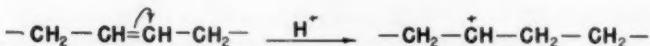
The present study on the structure of cyclized polybutadiene was undertaken in order to obtain additional information with respect to the question of the presence of polycyclic structures in cyclized rubbers. Polybutadiene was chosen for study instead of natural rubber on the basis that the absence of the side chain methyl groups would give a simpler cyclized structure. The presence of vinyl side chains formed from some 1,2-polymerization of butadiene is a complicating factor, but the predominance of 1,4-polymer chain segments should give rise to a major proportion of cyclized structures free of extraneous side chains.

Infrared analysis and changes in unsaturation were used to detect changes in structure during cyclization. The cyclized product was subjected to oxidative degradation and the nature of the residual high molecular weight acids suggested the presence of fused polycyclic structures.

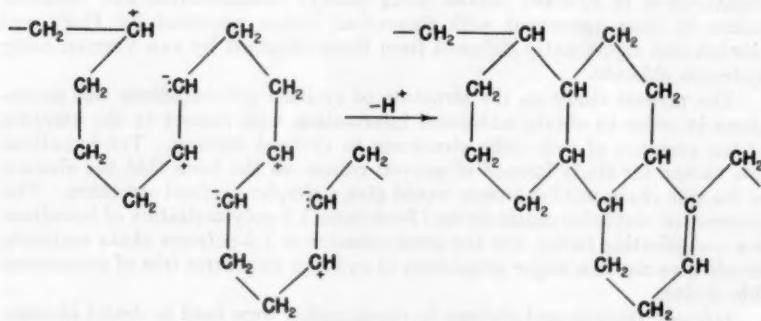
MECHANISM OF CYCLIZATION

Cyclization is considered to occur by a polar mechanism^{5,12} induced by an electrophilic reagent. For example, when an acid is used as the cyclizing agent, a proton adds to form a carbonium ion which in turn polarizes, and ultimately combines with a double bond in an adjacent butadiene unit to form a six-membered ring:

* An original contribution.



The cyclic carbonium ion may lose a proton to form a cyclohexene ring, or the reaction may repeat by activation of the unsaturation in the next 1,4-butadiene unit and thus propagate the reaction through additional steps to form a fused polycyclic structure. The termination step is considered to be a slow deprotonation process resulting in a double bond somewhere in the ring, but the exact location is uncertain. The mechanism thus predicts the possible formation of polycyclic structures such as II in the following reaction:



I

II

Statistically it has been estimated for natural rubber that about 13 per cent of the mer-units are left uncyclized⁶. Cyclized rubbers can thus be regarded as copolymers of cyclized segments (whether mono or polycyclic) with some uncyclized segments.

The first step in the hydrochlorination of rubber is likewise the addition of a proton to form a carbonium ion. Gordon and Taylor⁷ present evidence in support of a cyclic intermediate complex for the next step of the reaction to account for the stereochemical orientation of successive units in rubber hydrochloride. Their cyclic intermediate is analogous to I above except that HCl

adds to reopen the cyclic complex simultaneously with the activation and temporary cyclization of the next unit of the chain.

The ease of cyclization is affected by the presence of substituent groups. The energy of activation for the cyclization of natural rubber has been calculated from kinetic data at several temperatures^{5,6} and is reported to be 32.7 kcal. However, the presence of a methyl group in place of hydrogen has been calculated to increase the proton affinity of a C=C group by 13.5 kcal. Thus the activation energy for the cyclization of polybutadiene should be correspondingly higher than for natural rubber and would account for the greater difficulty encountered in cyclizing this synthetic rubber.

Analogous structures are encountered frequently in related fields of organic chemistry. It has been suggested that the cyclic terpenes⁴ are formed by cyclizing isoprene units into higher molecular weight structures including polycyclic compounds such as α -amyrin¹². The cyclization of ω -geranyl-geranic acid to form a tricyclic acid¹ is another example of the formation of polycyclic compounds from polyenes.

EXPERIMENTAL

Raw material.—The polybutadiene used for this study was obtained from the Government Rubber Laboratory in Akron, Ohio. It was polymerized at 122° F.

Cyclization procedure.—Polybutadiene (6.2 g) was dissolved in thiophene-free xylene (200 g) to form a 3 per cent solution which was placed in a one l three-necked flask. The solution was heated to the boiling point (140° C), while the temperature of the heating mantle was carefully controlled to prevent local overheating. Concentrated sulfuric acid (1.9 g) was added gradually with efficient stirring. During the course of reaction, small samples were removed from the flask and tested by mixing with a few ml of acetone. The completely cyclized polymer formed a powdery precipitate instead of an elastic substance. The reaction usually took about eighteen hours.

Some insoluble product (0.4 g) was formed presumably as a result of crosslinking. The conditions cited in the above procedure were selected on the basis of experience to give the minimum of insoluble product. After filtration, the solution of cyclized polybutadiene was refluxed with dilute NaOH for one hour to remove any trace of catalyst. The solution was washed in a separatory funnel with distilled water to remove the alkali and then steam distilled to remove the xylene. The cyclized product separated out as a light cream-colored powder (5.9 g) which was then dried at 50° C under vacuum.

For analysis, cyclized polybutadiene was extracted with acetone to remove the antioxidant and then carefully dried under the same condition.

Determination of unsaturation.—The iodine-bromide method was used¹⁴ with a correction for the substitution which occurs as well as addition to the double bond. The reagents used were bromine (reagent grade), iodine (resublimed), carbon tetrachloride (redistilled), sodium thiosulfate (0.1 N), potassium iodide (10%) and potassium iodate (4%).

The purified cyclized polybutadiene was extracted with carbon tetrachloride to separate it from microgel. The weight of the polymer solution was determined by evaporating off the solvent from a 25 ml portion and weighing the solid content.

Twenty-five ml of the extract was pipetted into an iodine flask (250 ml).

After addition of 25 ml of iodine-bromide solution, the sample was allowed to stand for 30 minutes and then cooled in ice. The glass stopper of the flask was moistened with a few drops of potassium iodide solution. While cooling, 50 ml of distilled water was added gradually with thorough shaking. After the addition of 15 ml of 10% potassium iodide solution, the mixture was titrated immediately with 0.1 *N* sodium thiosulfate solution. At the end of the titration, 12.5 ml of alcohol was added to break the emulsion.

In order to determine the amount of acid liberated due to substitution, two ml of potassium iodate solution (4%) was added to the mixture. The reappearance of the bluish color indicated the presence of acid, and the titration was continued until the color faded. A blank solution was run in the same manner.

Infrared analysis of the polymer.—The acetone-extracted sample was dissolved in benzene to make a 1.5% solution. A steel frame was used to cast the film. An evaporating dish was filled with sufficient water to cover the frame and the benzene solution was carefully poured on top of the water. On slow evaporation of the benzene, a thin film of cyclized polybutadiene was deposited on the surface of the water. By careful lifting of the frame, a uniform film was obtained on the frame. The film was air dried before analysis on a Perkin-Elmer model 12C spectrophotometer.

Oxidation of cyclized polybutadiene.—Acidic potassium permanganate was selected for the oxidative degradation studies⁹. Chlorobenzene, used as the solvent, was purified by reacting with acidic permanganate solution and was redistilled before use.

A series of small-necked bottles (400 ml) were placed in a constant temperature bath equipped with a shaking device. In each bottle, cyclized polybutadiene (1 g) was dissolved in purified chlorobenzene (66 ml) with the aid of preheating at 90–100° C. After the solution was cooled down to room temperature, a potassium permanganate solution (4.9 g of KMnO₄ in 180 ml of water) and 15 ml of 2*N* H₂SO₄ was added to the bottle. The stoppered bottles were shaken at room temperature until the oxidation was complete as determined by the fading of the characteristic color of permanganate.

The mixture was filtered to remove the precipitated manganese oxide and water-insoluble organic product. The organic material proved to be soluble in dilute sodium hydroxide solution and was easily extracted in this manner from the inorganic residue. The original filtrate separated into two layers, and another portion of the water insoluble acid was obtained from the chlorobenzene layer by washing with sodium hydroxide solution.

The aqueous solution containing the sodium salt of the insoluble acid was concentrated, filtered, and acidified with hydrochloric acid (3*N*) to a pH of 2.5. The insoluble acid then was heated with water and washed free of hydrogen chloride. After drying it was dissolved in acetone and filtered to remove inorganic salts. The solvent was then evaporated to recover the organic material which was then washed with benzene to remove any unoxidized starting material.

The insoluble acid (0.15 g) was further purified to give a powder with a melting point of 154–156° C. It was analyzed for carbon and hydrogen and the molecular weight determined by the Rast method. Titration with standard base gave a neutralization equivalent corresponding to that of a dibasic acid.

Analysis for C₁₆H₂₂O₄.—Calc'd: C, 69.07; H, 7.91; O, 22.99; M.W. 278; Neutr. Equiv. 139. Found: C, 69.15; H, 7.71; O, 23.14; M.W. 282; Neutr. Equiv. 139.

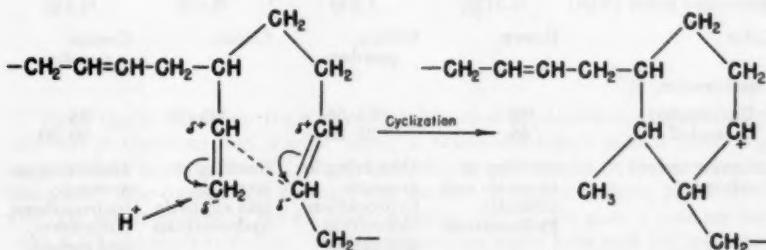
Oxidation of polybutadiene.—Acidic potassium permanganate was also used to degrade uncyclized polybutadiene. The procedure was the same as above except for the quantity of permanganate solution.* For one g of polybutadiene in 66 ml of chlorobenzene, 8.2 g of postassium permanganate in 300 ml of water and 26 ml of 2*N* H₂SO₄ were used. No insoluble acid was found after oxidation under conditions comparable to those employed for the cyclized material.

Ozonization of the water-insoluble acid.—The insoluble acid (1 g) obtained from a subsequent oxidation of a larger quantity of cyclized polybutadiene was dissolved in glacial acetic acid (100 ml). The solution was subjected to ozonization. After the solution ceased to absorb any more ozone, it was filtered and the glacial acetic acid was distilled off. Addition of distilled water to the residue precipitated the ozonized products. The mixture was heated on a steam bath. The precipitate was filtered off and washed free of acetic acid and dried. The product (m.p. 164–166° C) was an amorphous powder, soluble in dilute base but insoluble in water, which evolved gas above 170° C and gave a positive carbonyl group test with *p*-nitrophenylhydrazine. The amount of material obtained was not sufficient to permit further study.

RESULTS AND DISCUSSION

The cyclization of polybutadiene was known to be more difficult than that of natural rubber, and consequently, rather drastic conditions were employed for the initial experiments. Considerable insoluble, and presumably cross-linked, material was obtained. This undesirable side reaction was minimized in subsequent work by using a more dilute solution of polybutadiene with careful temperature control to prevent local overheating.

The side-chain vinyl groups resulting from some 1,2 polymerization of butadiene are probably involved in the crosslinking reaction since a carbonium ion on one chain might be expected to add to such a group on another chain more readily than to an internal double bond. This would account in part for the decrease in intensity of the band for this group in the infrared spectrum after cyclization (Table I). The vinyl groups must also be involved in the cyclization reaction, however, in view of the marked decrease even when the crosslinking was kept to a minimum. The structural irregularity introduced by the 1,2 isomer would be expected to interrupt the propagation of the reaction leading to polycyclic structures.

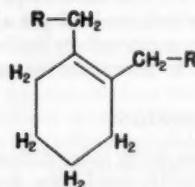


The decrease in total unsaturation as reflected in the infrared spectrum is very marked as shown in Table I. The weak absorption observed after cyclization can only be attributed to the presence of some uncyclized chain

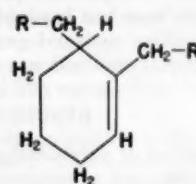
TABLE I
CHANGES OF THE INFRARED SPECTRUM AFTER CYCLIZATION
OF POLYBUTADIENE

Structural groups	Bands (μ)	Before cyclization	After cyclization
C=C	6.10	strong	very weak
R—CH=CH ₂ (vinyl group)	10.15	strong	weak
R—CH=CH—R	11.00	strong	weak
	10.30	strong	weak

segments. Since the absorption is so weak for the cyclized polybutadiene the unsaturation present in the rings must be predominately of the tetra-substituted type which does not show in the infrared spectrum. Thus, cyclo-olefin structures of the type represented by III seems more probable than IV. If IV is formed it could readily isomerize to III in the presence of an acid catalyst.



III



IV

Interpretation of unsaturation data for polymers is open to question as shown by the conflicting evidences already cited^{12,13}. Nevertheless, changes in unsaturation were measured using the Vasilev iodine-bromide method¹⁴.

TABLE II
COMPARISON OF PHYSICAL PROPERTIES OF UNCYCLIZED
AND CYCLIZED POLYMERS

Properties	Polybutadiene		Natural rubber	
	Uncyclized	Cyclized	Uncyclized	Cyclized
Specific gravity (d_4^{25})	1.090	1.07	1.092	1.12
Refractive index (N_D^{25})	1.512	1.540	1.520	1.545
Color	Brown	Cream powder	Cream	Cream powder
Unsaturation, %				
Uncorrected	88	54-56	95-96	55
Corrected	88	25-28		20-30
Behavior toward solvents	Swelling in aromatic and aliphatic hydrocarbons	Dissolving in aromatic hydrocarbons, chloroform and carbon tetrachloride	Swelling in aromatic and aliphatic hydrocarbons	Dissolving in aromatic hydrocarbons, chloroform, and carbon tetrachloride

¹ D'Ianni, *Ind. Eng. Chem.*, **40**, 263 (1948).

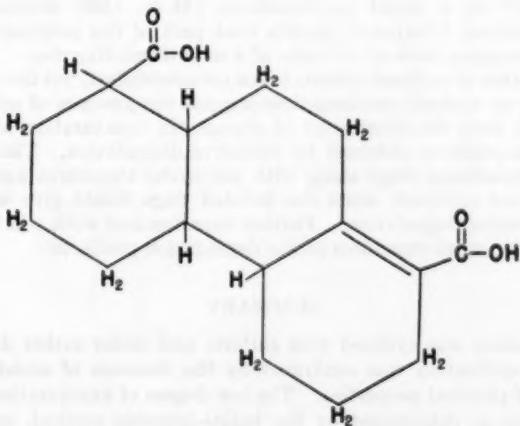
² D'Ianni, *Ind. Eng. Chem.*, **38**, 1171 (1946).

³ Determined by the iodine-bromide method.

⁴ Determined by the iodine-chloride method.

It is a double titration method in which the total consumption of halogen for addition and substitution is determined in the first step, and then the amount of halogen consumed by substitution is measured in the second step by finding the equivalent of the hydrogen ion formed. Both polybutadiene and cyclized polybutadiene were analyzed by this method. The results are given in Table II along with a comparison of other properties of cyclized and uncyclized polybutadiene and natural rubber. No evidence of substitution was observed in the case of uncyclized polybutadiene. The values obtained for cyclized polybutadiene after correction for substitution are consistent with a structure built up of polycyclic condensed rings, rather than isolated six-membered rings. In view of the questionable validity of the unsaturation measurements, the structure of the cyclized product was also studied by oxidative degradation.

Several methods of oxidative degradation were investigated, but potassium permanganate proved to be most satisfactory in this case. Both polybutadiene and the cyclized product were subjected to oxidation. A water-insoluble acid was isolated from the oxidation products of cyclized polybutadiene but not of polybutadiene. The acid gave an elementary analysis, molecular weight, and neutralization equivalent corresponding to a dicarboxylic acid with the formula, $C_{16}H_{22}O_4$. These data, together with predictions based on a polar mechanism of cyclization suggested the following structure:

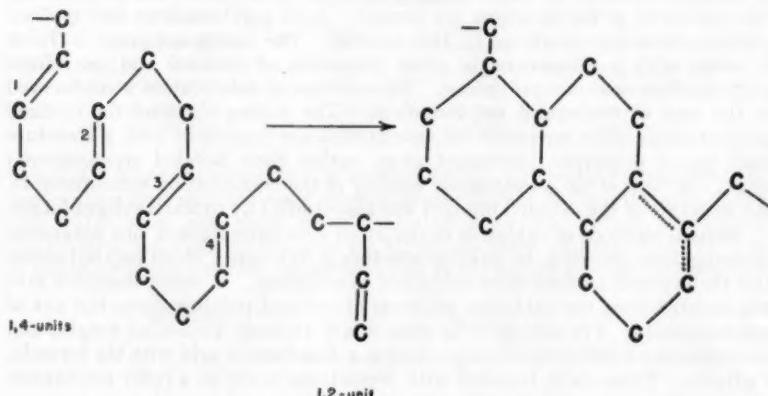


V

Since the infrared spectrum showed evidence of a possible conjugated acid, but not a trisubstituted double bond, a tetrasubstituted double bond was suggested as in structure V. Further evidence was sought by ozonization of the acid. The ozonization product was an acid of higher melting point (164–166° C) which evolved a gas on heating above 170° C and gave a positive test with *p*-nitrophenylhydrazine. This suggested an alpha keto acid (as predicted for the ozonization of structure V) which would decarboxylate on heating.

The formation of a tricyclic ring system is reasonable since the uncyclized material contained approximately 20 per cent of 1,2 polymer units. Thus, four

out of five "mer" units would be 1,4 units and just sufficient to form a 3-ring system by van Veesen's mechanism:



Literature¹⁰ on a liquid polybutadiene (M.W. 1500, developed by the Phillips Petroleum Company) reports that part of the polymer is cyclized. Ultraviolet scanning showed evidence of a naphthenic-like ring.

The structure of cyclized rubbers is not yet established, but the observations in this study on cyclized polybutadiene suggest the presence of polycyclic ring systems both from the standpoint of changes in unsaturation and from the nature of the products obtained by oxidative degradation. The presence of isolated six-membered rings along with polycyclic structures and uncyclized segments is not excluded, since the isolated rings would give water soluble acids on oxidative degradation. Further experimental work will be necessary to establish the exact structures of the degradation products.

SUMMARY

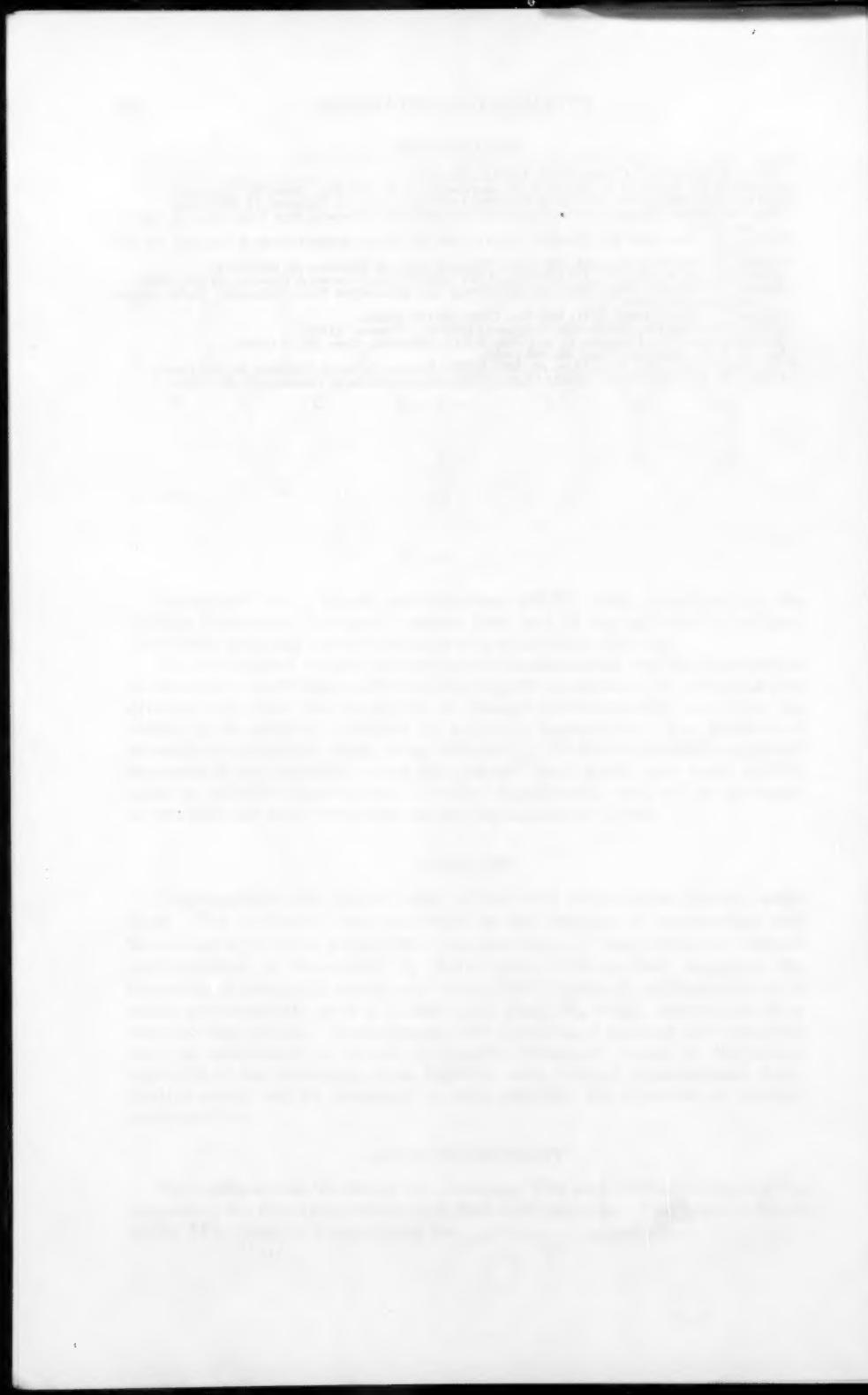
Polybutadiene was cyclized with sulfuric acid under rather drastic conditions. The cyclization was confirmed by the decrease of unsaturation and the change of physical properties. The low degree of unsaturation of cyclized polybutadiene, as determined by the iodine-bromide method, suggested the formation of polycyclic structures. Oxidation of cyclized polybutadiene with acidic permanganate gave a dibasic acid, $C_{16}H_{22}O_4$, which corresponds to a tricyclic ring system. Consequently, the structure of cyclized polybutadiene may be considered to include polycyclic structures joined by uncyclized segments of the molecular chain together with isolated six-membered rings. Further study will be necessary to fully establish the structure of cyclized polybutadiene.

ACKNOWLEDGMENT

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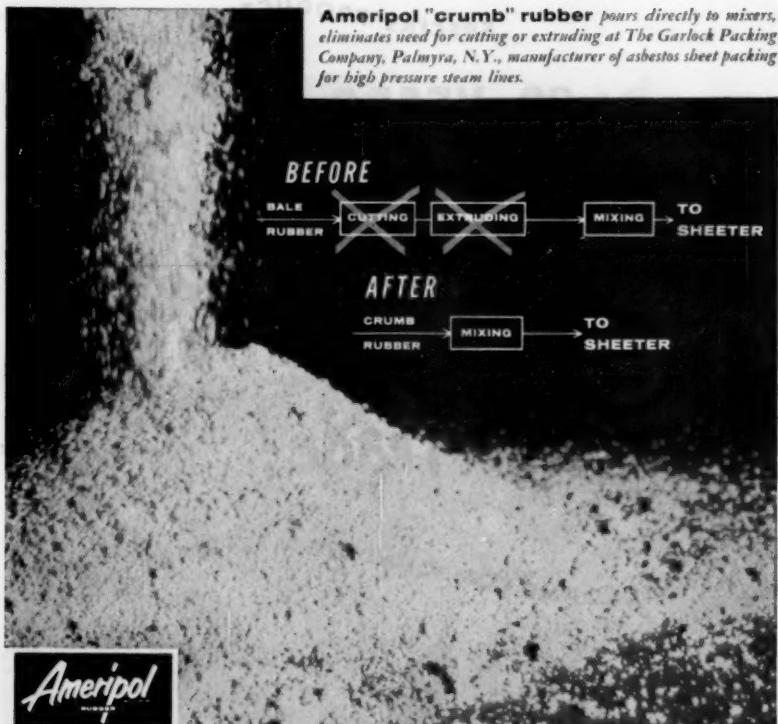


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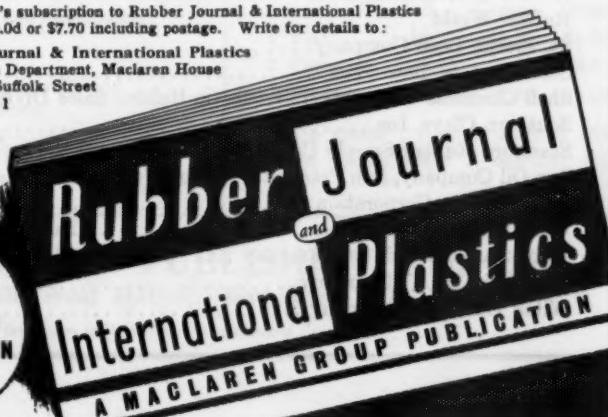
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